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FLAME RESISTANT FIBROUS MATERIALS

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ABSTRACT

Four chlorofluoropolymer systems that satisfactorily met the criteria for classification as self-extinguishing, in accordance with the procedures of Category A, MSC-PA-D-67-13, were developed. Three of these systems consisted of Halar (a copolymer of chlorotrifluoroethylene and ethylene) and tin-based flame retardants. The fourth system was a copolymer of chlorotrifluoroethylene and tetrafluoroethylene with no flame retardants added. Production of fibers from all four candidates, by melt extrusion, was demonstrated. Fibers produced from the chlorotrifluoroethylene-tetrafluoroethylene copolymer showed the most promise.

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NOMENCLATURE

D	=	Agitator Diameter
I	=	Polymerization Initiator Concentration
K	=	Initiator Decomposition Reaction Rate Constant
M	=	Vapor Space Monomer Concentration
m	=	Copolymer Composition
N	=	Agitator Speed
R.	=	Free Radical Concentration
Re	=	Reynolds Number $= \frac{D^2 N \rho}{\mu}$
r	=	Reactivity Ratio
ρ	=	Reactor Fluid Density
μ	=	Reactor Fluid Viscosity

FLAME RESISTANT FIBROUS MATERIALS DEVELOPMENT

CONTRACT NO. NAS 9-12257

INTRODUCTION

Historically, progress in advanced technical disciplines has been dependent on the rate of development of special materials of construction. The advent of the space age has markedly accelerated this rate. Specifically, the need for new flame resistant fabrics for applications such as spacesuit cover layers and flight coveralls has become apparent.

The fibers used in these constructions must meet the NASA requirements of non-flammability in enriched oxygen atmospheres, in addition to the fiber strength, weight per unit volume and heat resistance criteria. Thus far only inorganic fibers have qualified. However, they lack the abrasion resistance, durability and "hand" of common organic fibers such as nylon.

This report summarizes an effort to develop flame resistant fiber candidates from chlorofluoropolymers. In Phase I several candidates, with and without flame retardant additives, were screened. Preliminary fiber extrusion tests were also conducted. Phase II was devoted to developing production techniques for and determining the engineering properties of a new chlorofluoropolymer that showed promise as a flame resistant material of construction.

SUMMARY

Four chlorofluoropolymer systems that satisfactorily met the criteria for classification as self-extinguishing in an environment of 70% oxygen and 30% nitrogen at 6.2 PSIA total pressure were developed. The flammability tests were conducted by NASA in accordance with the procedures of Category A, MSC-PA-D-67-13.

These systems included:

- Halar (copolymer of chlorotrifluoroethylene and ethylene) plus 15% stannic oxide hydrate.
- Halar plus 10% stannous oxalate.
- Halar plus 5% stannous phosphate.
- A copolymer of chlorotrifluoroethylene (CTFE) and tetrafluoroethylene (TFE) in the composition range of 40 to 70 mol % CTFE and 60 to 30 mol % TFE. This material, referred to as the ECS copolymer, contained no stabilizers or flame retardant additives.

Production of fibers from all four candidates by melt extrusion was demonstrated. Fibers produced from the ECS copolymer showed the most promise.

A granular polymerization process was developed and used to produce copolymers of CTFE and TFE for evaluation of engineering properties. Copolymers containing 40-60 mol % of CTFE exhibited the outstanding electrical and chemical resistance properties characteristic of fluoropolymers.

CONCLUSIONS

A completely organic polymer has been developed which passes the NASA flammability requirements in enriched oxygen atmospheres when tested in accordance with MSC-PA-D-67-13. This polymer has been converted into multifilament yarns by conventional melt-extrusion techniques. Additional research will be needed to optimize fiber spinning and orientation techniques so as to obtain low denier, high tenacity fibers for fabric preparation.

Flame-retardant additives have been discovered that permit Halar[®], a commercial polymer made by Allied Chemical Corp., to successfully meet the NASA flammability requirements specified in this contract. Preparation of uniform, high strength fibers from these blends has not been accomplished to date.

RECOMMENDATIONS

Develop spinning and drawing techniques for converting ECS copolymers into fine denier, high tenacity multifilaments.

Pursue development of Halar[®] fiber for those spacecraft applications where less stringent oxygen environments have been specified.

EXPERIMENTAL - PHASE I

A. Objectives

The current flame resistant fibrous materials for use in oxygen environments are inorganic fibers. Although these fibers have met the NASA requirements for non-flammability in enriched oxygen atmospheres, they lack the abrasion resistance, durability and "hand" of conventional organic fibers. All known organic fibers had been found to be unsatisfactory when tested for flammability in accordance with the upward propagation test per Category A, MSC-PA-D-67-13. The objectives of Phase I were to first develop one or more organic polymers that would meet the non-flammability requirements and then to prepare fibrous structures from the best polymer candidate for applications in spacecraft as spacesuit cover layers, flight coveralls, restraint webbings, storage containers, etc.

To be considered acceptable for these applications, the fiber candidate should, in addition to meeting the non-flammability criteria, have the following properties:

Physical Properties:

1. Denier Required	2-10
2. Breaking Tenacity gpd	4-6
3. Elongation, %	10-30
4. Specific Gravity	1.3-2.1
5. Stiffness, gpd	10-30
6. Resistance to Heat	Shall not degrade at 400°F

Other Requirements

1. Offgassing acceptable per MSC-PA-D-67-13.
2. Toxicity acceptable per MSC-PA-D-67-13.
3. Odor acceptable per MSC-PA-D-67-13
4. Effect of organic solvents: shall not be affected by common solvents.
5. Effect of vacuum: shall not have a weight loss exceeding 10% when the fiber is subjected to a vacuum pressure of 10^{-6} torr for 24 hours, nor shall it show signs of loss of flexibility, cracking or brittleness after subjection.

B. Technical Approach

The technical approach that was taken to achieve the Phase I objective of developing the polymer candidate was to investigate fluoropolymers with and without flame-retardant additives. It was reasoned that the stringent requirements of non-flammability in enriched oxygen atmospheres could be better met by chloro-carbon or chlorofluorocarbon-based polymeric structures rather than by hydrocarbons. Early in the contract it was established that the common fluorocarbon polymers could not meet the test criteria for non-flammability per MSC-PA-D-67-13. For this reason, various flame-retardant additives were incorporated into the polymers at different concentrations to enhance flame-retardancy. The selection of the flame-retardants was based on the known theories of flame retardancy in halogenated polymers with particular emphasis placed on antimony, nitrogen, phosphorous and tin based additives, keeping in mind the generally synergistic action of these compounds with halogenated moieties.

Phase II of the study was originally intended to provide textile fabrics prepared from the best polymer candidate developed in Phase I. Since the polymer developed in Phase I was only on test tube scale, this phase was subsequently modified, with the approval of NASA, to be the development of a pilot plant scale polymerization process to produce pound quantities of polymers for engineering property measurements.

C. Candidates

The Polymer candidates developed and tested for flammability per MSC-PA-D-67-13 could be grouped under three broad categories:

1. Commercial or developmental polymers without any flame retardants. These are listed below:
 - a. Polychlorotrifluoroethylene (PCTFE)
 - b. Chlorotrifluoroethylene-Vinylidene Fluoride Copolymer (VK)
 - c. Chlorotrifluoroethylene/Vinylidene Fluoride/Tetrafluoroethylene Terpolymer (TVS)
 - d. Polytetrafluoroethylene (PTFE)
 - e. Copolymer of Chlorotrifluoroethylene-Ethylene (Halar®).
 - f. Copolymer of Tetrafluoroethylene-Ethylene (Tefzel)
 - g. Tetrafluoroethylene/Hexafluoropropylene Copolymer (FEP®)
 - h. Tetrafluoroethylene/Perfluorovinyl-alkoxy Copolymer (PFA®)
 - i. Hexafluoroisobutylene-Vinylidene Fluoride Copolymer (CM-1)
2. Halar®, VK, TVS, PCTFE, and PTFE with 5-15% of flame retardant additives. Only in the case of Halar® was there a significant improvement in non-flammability when additives were incorporated. The additives that were evaluated were:
 - Tetraphenyl Tin
 - Barium Chloranilate
 - Hydrated Stannic Oxide
 - Thermolite 35
 - Stannous Oxalate
 - Tetramethyl Thiuram Disulfide
 - N,N'-Diphenyl-p-phenylene Diamine
 - 2,6-di-tert-butyl-4-methyl Phenol
 - Antimony Oxide
 - Red Phosphorous
 - Chlorinated Polyphenyls
 - Diphenylisodecyl Phosphite
 - Triphenyl Phosphite
 - Trilauryl Phosphite
 - Weston TP-24 (aromatic phosphite of 23.5% P)
 - Weston 465 (9.2% P)
 - Weston 467 (7.7% P)
 - Alumina Trihydrate
 - Stannous Phosphate, Tribasic
 - Stannous Pyrophosphate
 - Di-n-propyltin Dichloride
 - Triphenyl Tin Chloride
 - Tricresylphosphate
3. Research Polymers: For the purpose of flammability testing, small quantities of four experimental polymers were synthesized and attempts were made to synthesize two others. These were:
 - a. CTFE/ethylene 1:1 copolymer synthesized at very low (-78°C) temperatures.
 - b. Chlorinated Halar®

- c. CTFE/TFE copolymers of different compositions (ECS)
- d. CTFE/vinyl phosphonic Acid copolymer
- e. Stereoregular PCTFE
- f. CTFE-rich Halar® (55 to 75 mole % CTFE)

The results of the above three-pronged approach are summarized as follows:

1. Stannic oxide hydrate, stannous oxalate and tribasic stannous phosphate were found to render Halar® self-extinguishing per MSC-PA-D-67-13. Of these stannous phosphate was the most effective with levels as low as 5% sufficient to impart nonflammability.
2. Without the use of any additives the copolymer of CTFE-TFE in the composition range of 40 to 70 mole % CTFE and 60 to 30 mole % TFE passed the flame test. Polymers outside this composition range were not self-extinguishing.
3. Little improvement in flame-resistant was achieved by chlorinating Halar® up to about 30% level of chlorination.
4. Attempts to prepare stereoregular PCTFE were unsuccessful.
5. Halar® with the three effective additives could be melt-spun into fibers. However, additional work would be necessary to achieve the desired levels of mechanical strength.
6. The ECS copolymers could be spun into multi-filaments and cold drawn. They passed all NASA flammability requirements and gave off extremely low levels of smoke.

D. Preparation of Polymer Candidates

Halar® Blends with Flame-Retardant Additives:

Commercial grade Halar® powder of 0.5 to 4.0 M.I. was first blended with the additives in a ball-mill for 6 hours, then melt-blended in a Brabender Plasticorder for 10 minutes at 260°C at a screw speed of 50 RPM. No severe degradation or cross-linking of the polymer was noted as evidenced by constant torque values during the mixing period.

Chlorinated Halar®:

Finely pulverized unstabilized Halar® was slurried in a large excess of carbon tetrachloride and chlorinated for four hours at 65°C in an aqueous suspending medium of 37% HCl. Ultra-violet irradiation from a 500 watt mercury vapor lamp was admitted into the reaction flask during the chlorination. An azo photo-sensitizer was present in the organic phase during the reaction.

Chlorine and hydrogen analysis of the resultant polymer showed that the extent of chlorination was about 30%. The polymer melting point dropped from 242°C to 218°C and the crystallinity decreased about 25%.

Very Low-Temperature Polymerized CTFE/Ethylene Copolymer:

500 grams of CTFE were condensed into a 1 liter flask maintained at -78°C and ethylene gas was bubbled slowly through the liquid CTFE. One gram of tri-n-butylboron activated with a molal equivalent of oxygen was introduced and the reaction was carried out at -78°C to obtain 90 grams of polymer melting at 261°C with a melt index of 2.4 at 300°C .

Stereoregular PCTFE (Attempted Synthesis)

Liquid CTFE monomer at -78°C was reacted with oxygen-activated tri-n-butyl boron at -78°C , -50°C , -20°C and 0°C . Polymerization did not occur at any of these temperatures.

CTFE was reacted at -78°C using γ -irradiation from a Co^{60} source at a dose rate of 0.20 megarads per hour for 24 hours. Low molecular weight grease rather than solid polymer was obtained. Lowering the dose rate to 0.05 megarad per hour for 24 hours still yielded only a grease.

The binary catalyst system of tri-isobutylaluminum and tetraisopropyl titanate in methylene chloride solvent was used at -30°C and 0°C at Al/Ti mole ratios of 0.5, 1.0 and 2.0. Only low melting (140°C - 145°C) low molecular weight polymers were prepared at 25°C with an Al/Ti mole ratio of 2:1.

CTFE/Vinylphosphonic Acid Copolymers

CTFE was copolymerized in an autoclave with 3 mole % of vinylphosphonic acid at 0°C using trichloroacetylperoxide as a free-radical initiator. Copolymers containing about 10 mole % acid resulted. The polymer was amorphous and tacky with a softening temperature of 55°C .

CTFE/TFE Copolymers

The preparation of a typical copolymer is illustrated by the following procedure for a 50/50 copolymer:

Into a 1-gallon stainless steel autoclave was charged 2 liters of deaerated 1,1,2-trichloro-1,2,2-trifluoroethylene. The reactor was pealed, and evacuated. 500 grams of chlorotrifluoroethylene were condensed in, followed by enough tetrafluoroethylene gas to obtain a liquid phase composition of 50 mole % of each monomer. An organic peroxide initiator dissolved in 100cc of chloroform was introduced and the reaction was carried out for 6 hours. At the end of this period, the reactor was vented and evacuated. The polymer was discharged as a thick slurry in the solvent. It was filtered, washed with excess methanol and dried for 20 hours to obtain 300 grams of polymer melting at 242°C . The polymer analyzed to approximately 50 mole % of each monomer and had a melt index of about 4.2 at 300°C and with a load of 2160 grams.

E. Test Specimen Preparation

5" x 3" x 10 mils thick films were compression molded at about 30°C above the polymer melting temperatures in a Carver press using a 10 mil stainless-steel die. The molded film was cooled

in air rather than quick-quenched in water in order to avoid or minimize surface roughness due to excessive shrinkage. The use of any mold-release agents was avoided as much as possible so as to eliminate any possible effect they might have on flammability. The compression molded films were labelled and mailed to MSC (Houston) for upward propagation rate test per MSC-PA-D-67-13.

F. Test Procedures

Upward Propagation Rate Test

The description of this test as published by NASA is shown in Appendix I.

Melt Index

An electrically heated melt index apparatus with a Hastaloy barrel and 1/16" carbon-steel die was used to measure melt indices of different polymers at test temperatures (generally about 30°C above the polymer melting temperatures). The results were expressed as grams flow per 10 minutes at the specified temperature and load (stress).

Limiting Oxygen Index

These values were measured on 5" x 1/4" x 1/8" strips of compression-molded polymer plaques per ASTM test procedure D 2863-70 using a CSI Oxygen Index Analysis fitted with a continuous oxygen monitor. The results were averaged for 10 specimens for each sample.

Differential Scanning Calorimetry (DSC)

Polymer melting points, crystallization points, and crystallinity were measured using a Perkin Elmer DSC unit at heating and cooling rates of 20°/minute.

Thermal Gravimetric Analysis (TGA)

Thermal stability of selected polymers were measured in nitrogen and in air using both isothermal and programmed heating in a Cal Balance TGA apparatus.

Thermomechanical Analysis (TMA)

Measurement of longitudinal elongation and shrinkage of spun filaments as a function of temperature was studied using a Perkin Elmer TMA unit at heating rates of 10°/minute in helium. The particle size measurement of flame-retardant additives (stannous oxalate and stannic oxide hydrate) was carried out using a Coulter Counter. The tensile properties of drawn and undrawn filaments were measured using an Instron tensile testing machine. The microstructure of polymers and copolymers was determined by elemental analysis for carbon, hydrogen, chlorine and, in a few cases, fluorine. Information on mole percent ethylene blocks in Halar and inchlorinated Halar was obtained using near-infra-red spectroscopy (Ref. 3). Filament spinning trials were performed using (a) a ram extruder and (b) a 1/2" dia. 22:1 L/D Reifenhauer Screw Extruder.

G. Results and Discussion

Table I lists the flammability test data per MSC-PA-D-67-13 on various Halar -additive blends. It is seen that three inorganic tin compounds, namely stannic oxide hydrate ($\text{SnO}_2 \cdot x \text{H}_2\text{O}$ where $x = 1$ to 1.5), stannous oxalate ($\text{Sn}(\text{COO})_2$) and tribasic stannous phosphate ($\text{Sn}_3(\text{PO}_4)_2 \cdot x \text{H}_2\text{O}$ where $x = 1$ to 2) rendered Halar self-extinguishing. It is known from flame-retardation of other polymers such as PVC, polyethylene and polypropylene that hydrated stannic oxide is as effective a flame-retardant as antimony oxide. However, in the case of Halar, stannic oxide hydrate was much more effective than antimony oxide. The most effective flame-retardant additive was tribasic stannous phosphate. This led to the expectation that there might be a tin-phosphorous-halogen synergism at work. This postulate could not be sustained when stannous pyrophosphate was substituted for the tribasic stannous phosphate. The former failed to render Halar® self-extinguishing even at 10% levels while the latter sufficed at as low as 50%. It is reasonable to expect that the water of hydration in both $\text{SnO}_2 \cdot x \text{H}_2\text{O}$ and $\text{Sn}_3(\text{PO}_4)_2 \cdot x \text{H}_2\text{O}$ might be playing a part in the flame retardation mechanism. Even though stannic oxide hydrate loses almost a mole of water per mole when heated to 225°C , some of the water of hydration is still present even at 475°C . Tribasic stannous phosphate might retain higher levels of water at these higher temperatures, thus making it the most effective additive. However it is difficult to explain the results completely from the point of view of the retention of water of hydration. In the case of stannous oxalate, formation of CO_2 at the combustion temperatures might provide a cooling and quenching zone, in addition to the fire retardancy contributed by stannous halides and other volatile stannous compounds that may have formed during burning. The results showed that organotin compounds were totally ineffective as fire retardants in contrast to the inorganic tin salts. Compression-molded films from the blends of Halar® with the three tin salts were free of bubbles or degradation and no difficulties were encountered either in melt-blending or molding thin films.

Table II shows the limiting oxygen index numbers measured on Halar blends with the three tin compounds as well as Sb_2O_3 and red phosphorous. These tin compounds not only rendered Halar self-extinguishing in the NASA flame test but also improved its oxygen index considerably.

Halar® blends with all three tin salts, while passing the flame propagation test, give off substantial amounts of smoke and soot during burning.

Table III presents test data on flammability of polymers without any flame-retardant additives. The CTFE/TFE copolymers are listed separately in Table III. All the polymers listed failed the propagation rate test. It is interesting to note that both PCTFE and PTFE, with oxygen index values of 98 and 95 respectively, failed to meet the criteria for non-flammability in the NASA test.

Synthesis data on CTFE/TFE copolymers are shown in Table IV. Polymers of any desired composition or molecular weight could be easily prepared by adjusting feed monomer composition and chloroform concentration. Table V listed the test results on upward propagation rate per MSC-PA-D-67-13. The range of compositions over which these copolymers passed the test criteria for classification as self-extinguishing was approximately 40 to 70 mole % CTFE and 60 to 30 mole % TFE. These copolymer compositions provided, for the first time, a completely organic material capable of being made into fibrous structures, which was serviceable in enriched oxygen atmospheres. These copolymer were surprisingly clean burning in the sense that very little smoke or soot was emitted when they were burned. Normally, the copolymer melted and flowed away. The drops self-extinguished as they fell.

Since both PCTFE and PTFE failed the flammability test whereas the copolymers passed, it was probable that one reason for this could be a difference in the thermal degradation mechanisms of the copolymer and the two homopolymers. To gain some insight into this, samples of Halar, CTFE/TFE copolymer, PCTFE and PTFE were analyzed by TGA in oxygen and nitrogen atmospheres and the results compared in Table VI. Halar, PCTFE and PTFE lost more weight in oxygen than in nitrogen, while the copolymer lost less weight in oxygen than in nitrogen. This indicated a possible difference in the mode of decomposition of the copolymer. Pyrolysis gas chromatography-mass spectrometry on PTFE, PCTFE and the copolymers showed that the major degradation products were:

<u>Polymer</u>	<u>Major Degradation Products</u>
PCTFE	CO ₂ , CF ₄ , CF ₃ Cl, Carbon
PTFE	CO ₂ , CF ₄ , C ₃ F ₈ , C ₄ F ₁₀
CTFE/TFE	CO ₂ , CF ₄ , CF ₃ Cl

H. Preliminary Fiber Production - Ram Extruder

Melt-spun Fibers From Halar®/Additive Blends

This work was done in a ram extruder using very finely powdered additives in Halar® blends. Halar® + 15% SnO₂ · x H₂O blends were ram extruded at 265°C using a 19 mil die. Melt draw-down was limited due to non-uniformity of additive dispersed in the polymer. The extrudate was capable of being drawn 5:1 at 125°C. Fiber properties were: tenacity 0.76 gpd; UE; 2.1% and TM: 34.2 gpd.

Halar® + 10% stannous exalate

Blends were ram-extruded using a 19 mil die. Examination of fiber showed opaque and transparent areas indicating non uniformity of dispersion. The fiber was drawn 5.3:1 at 125°C. Non-uniform draw was a problem. The fiber properties were tenacity 1.19 gpd; UE 4.65% and TM; 41.6 gpd. Halar + 10%

stannous phosphate blends were extruded as before. The fiber was capable of being drawn but premature breaks due to surface non-uniformity resulted in very poor draw-ratios and weak fibers.

After many ram extruder spinning trials with different levels of these three additives in Halar, it was obvious that under the conditions of our spinning experiments high degrees of melt draw-down and orientation could be attained to produce fibers of satisfactory mechanical strength and fineness of diameter.

Ram-extruder spinning trials were carried out on various CTFE/TFE copolymers listed in Table VII. Based on these results the following conclusions could be reached.

1. Resins of melt index less than about 1.0 could not be processed due to melt fracture and extrudate inability to draw-down in the melt.
2. The greatest melt draw-down potential was exhibited by 50/50 copolymers with melt index of about 4 but hot drawing of this fiber was not possible. Cold drawing about 5:1 yielded tenacities of less than 0.75 gpd. A typical set of properties for this fiber would be:
UTS = 0.52 gpd; UE = 16% and TM= 11.6 gpd.

I. Screw Extruder Tests

Screw Extruder Spinning Trials on CTFE/TFE Copolymers

All experiments were performed utilizing a 1/2" dia. 22:1 L/D Reifenhauer screw extruder. Figure I illustrated the essential features of the spinning assembly and the location of the various temperature zones and pressure gauges. Extruder components were constructed from stainless steel 416 and chrome plated to conform to recommended materials of construction. Filter screens, pressure gauges, and metering pumps were constructed from Hastaloy "C". This material has a high coefficient of expansion and poor polymer-lubrication characteristics. Thus, the pump tolerances were increased and the pump face and backing plates were chrome plated to prevent scoring.

Figure I illustrated the essential features of the spinning assembly and the locations of the various temperature zones and pressure gauges. Polymer was carried and mixed by a gradual transition screw with a compression ratio of 3:1, through a breaker plate containing 2-100 mesh Hastaloy "C" screens, and into the block assembly. The melt passed through the block where pressure was determined and flowed to the Zenith metering pump. The pump relayed the polymer at a constant rate, through the block and into the spin pot where it diverged over a filter screen pack containing 1-80 mesh and 3-100 mesh Hastaloy "C" screens. The pressure was recorded in the channel connecting the metering pump and filtering system. The melt passed through the screen pack and

converged through a short channel where the melt temperature and die pressure were measured. The melt then diverged over the die plant and was forced through the die orifice into the quenching media where the molten filaments were solidified.

Two quenching systems were employed in fiber preparation. One system was used for yarn and the other for monofil production. The quench stack assembly as shown in Figure I was employed for yarn production.

Upon exiting the die the molten yarn passed first through a 10" heated sleeve maintained at 240°C. The purpose of this heated sleeve was to maintain the yarn in a molten state which was necessary to achieve uniform melt draw-down without appreciable orientation. After passing through the sleeve the fiber was quenched by air traveling first perpendicular to the yarn path and then concurrently with the yarn. The air velocity and temperature were recorded and controlled to insure a stable process. The water system used to quench monofil is illustrated in Figure III.

Monofil traveled 20" through air before quenching. In the zone between the die and water level the monofil diameter was reduced to the desired level before quenching in water maintained at 45-50°C. Decreasing this distance resulted in a non-uniform thinning, and a decrease in water temperature lead to the formation of voids within the fil. It was possible to decrease the distance between the die and water level by increasing the water temperature to 76°C without effecting the quality of the monofil. Two take up systems were employed. One system, Figure II, was used in yarn production while the other, Figure III, was utilized for monofil.

Upon exiting the quench stack, the yarn passed through a drip gate and contacted a lube roll to pick up spin finish which was required to reduce the yarn's static charge and to reduce sliding friction between the yarn and draw pin. The yarn then passed over two rolls, the second of which was traveling 1% faster to insure uniform tension of filaments on the take up package. The speed of these rolls in conjunction with the extruder throughput determined the undrawn fiber denier. After passing through the water bath the fil passed through a nip roll assembly. The surface speed of this assembly in conjunction with the flow rate of molten polymer controlled the monofil denier. The film was collected by means of a Leesona winder. The majority of drawing experiments were performed using a heated pin/block assembly which was referred to as air drawing. This procedure was used for all yarns and monofil 15 mils. For monofil 15 mils a heated oil bath containing a submerged pin was employed to insure uniform heat transfer. This system was referred to as oil drawing. Air drawing as used for yarn and low diameter monofil was illustrated in Figure IV.

The undrawn fiber was pulled off the end of the package introducing 1/2 twist per foot and passed through a tension gate. This gate served primarily as a fiber guide to the pretensioning rolls whose diameter was 1% less than the feed godet. The pretensioning rolls and feed godet rotated at the same RPM but consequently the fiber was under the required tension to prevent slippage. The fiber was wrapped over the feed godet, heated pin, which controlled the position of the fiber neck, and passed over the surface of a 7" heat block. The fiber was then wrapped on the take up godet and passed to the winder where it was collected. The fiber draw ratio was determined by the difference between the surface speed of the take-up and feed godets. Oil drawing as illustrated in Figure V was used to monofil drawing for monofils 15 mils in diameter.

The undrawn monofil was rolled off the package introducing no twist and through a tension gate. The fiber was then wrapped on the feed godet and draw pin which was submerged in the oil bath. It then passed over several guides to the take up godet, through a wash bath to remove oil and was collected. Draw ratio was again determined by the speeds of the feed and take up godets.

The results of the multifilament spinning trials on 1.2 to 1.5 M.I. resins were:

1. All the resins were extrudable with little difficulty at $310^{\circ} - 320^{\circ}\text{C}$ using a 30 hole spinneret of 30 mils diameter.
2. Shear rates of about 125 sec^{-1} yielded extrudates free of melt-fracture.
3. Samples collected by air-quenching could not be drawn hot or cold after take-up.
4. Ice water quenching appeared to prevent total yarn crystallization but drawing after take-up was not uniform resulting in premature breaks and limited draw ratios of less than 2:1.
5. Filament deniers were higher than 200 mainly due to the fact that melt draw-down ratios were low. Additional work will be necessary to produce five denier fibers.
6. The effect of molecular weight distribution on melt-spinning in screw extruder was studied by extruding two copolymer (50/50 C/T) resins each of 4 M.I. but one of relatively narrow and the other of wider molecular weight distributions. Both resins extruded easily to give melt-fracture free extrudates at 300°C . Further work needs to be done to improve melt draw-down and ability to cold-draw.

Tables VIII and IX presented the results of isothermal and programmed TGA in air and in nitrogen of filaments prepared from CTFE/TFE copolymers of various compositions and melt-

indices. Thermal analysis of the CT copolymers of varying compositions and melt indices indicated the following:

1. The melting point and the thermal and oxidative stability increased with the TFE concentration.
2. In N_2 , the higher the M.I., the lower the stability, as expected. In air, the opposite was shown: the apparent weight loss was lower for the higher M.I. samples. This was, however, misleading, since in reactive atmospheres weight gain and loss occurred simultaneously, and the lower viscosity copolymers oxidized more readily.
3. Heat treatment at $350^\circ C$ was not favorable. The two copolymers (CT-27 and CT-31) used in the quenching, studies, showed insignificant changes when reheated after quenching, but the melting peak shape became broader, its length shorter and the T_m lower upon reheating after $350^\circ C$ quenching (most likely due to morphological changes). The isothermal TGA at $350^\circ C$, in both media, showed small weight loss (less than 1%), but also bubble formation, which was detrimental for drawing. Apparently $350^\circ C$ was too high a temperature for processing.

To understand why difficulty was encountered in drawing above room temperature, thermomechanical analysis (TMA) was carried out at $10^\circ C/\text{minute}$ in helium from room temperature to $150^\circ C$. The data indicated poor uniformity: The amount of shrinkage or elongation of the samples differed significantly; e.g., in the $40^\circ C$ to $95^\circ C$ temperature range, one piece of filament showed a 0.22% shrinkage while another showed a 1.3% elongation. Over the studied interval (from $25^\circ C$ to $150^\circ C$) the ratio of the maximum and minimum elongation was 6:1. Upon heating the lengths of the fibers become non-uniform. This was probably one of the factors which caused difficulty in drawing. Table X showed the detailed results of the TMA analysis.

TABLE I
RESULTS OF FLAMMABILITY TESTS
Silicone Ignitor; 6.2 PSIA 70% O₂ 30% N₂

<u>Sample</u>	<u>Flame Propagation Rate (inches/sec.)</u>
HALAR + 5% Stannous Oxalate	0.12
HALAR - 10% Stannous Oxalate	0.02
HALAR - 5% DM-8277	0.25
HALAR - 10% DM- 8277	0.20
HALAR - 5% Tetraphenyltin	0.12
HALAR - 10% Teltaphenyltin	0.45
HALAR - 5% Hydrated Tin Oxide	0.12
HALAR - 10% Hydrated Tin Oxide	0.012 (SE)
TVS - 10% Hydrated Tin Oxide	0.217
TVS - 10% Tetraphenyltin	0.625
HALAR - 5% Barium Chloranilate	0.18
HALAR - 5% Thermolite 35	0.17
HALAR - 5% Tetramethyl Thiuram Disulfide	0.11
HALAR - N,N-Diphenyl-p-phenylene Diamine	0.38

TABLE I - Continued

<u>SAMPLE</u>	<u>Flame Propagation Rate</u> <u>(Inches/Sec.)</u>
HALAR - 7.5% SnO ₂ . xH ₂ O	0.200
HALAR - 10% SnO ₂ . xH ₂ O	0.217
HALAR - 15% SnO ₂ . xH ₂ O	0.03 (SE in 3")
HALAR - 5% Sb ₂ O ₃	0.263
HALAR - 10% Sb ₂ O ₃	0.227
HALAR - 10% Sb ₂ O ₃	0.263
HALAR - 15% Sb ₂ O ₃	0.357
HALAR - 15% Sb ₂ O ₃	0.217
HALAR - 5% SnO ₂ . xH ₂ O - 5% Sb ₂ O ₃	0.200
HALAR - 5% SnO ₂ . xH ₂ O - 5% Red Phosphorous	0.384
HALAR - 5% SnO ₂ . xH ₂ O - 10% Aroclor	0.142
HALAR - 5% 2,6-di-tert-butyl-4-methyl phenol	0.217

TABLE I (cont'd)

<u>Sample</u>	<u>Flame Propagation Rate ("/Sec)</u>
HALAR - 5% Di-n-propyltin dichloride	0.238
HALAR - 10% Di-n-propyltin dichloride	0.247
HALAR - 15% Di-n-propyltin dichloride	0.250
HALAR - 10% Triphenyltin Chloride	0.450
HALAR - 10% Tricresylphosphate	0.625
HALAR - 4% Stannous Phosphate	0.022
HALAR - 3% Stannous Phosphate	0.166
HALAR - 2% Stannous Phosphate	0.33
HALAR - 1% Stannous Phosphate	0.25
HALAR - 5% Stannous Pyrophosphate	0.25
HALAR - 10% Stannous Pyrophosphate	0.20

TABLE I (contd)

Sample	Flame Propagation Rate (inches/sec.)
<hr/>	
HALAR - Diphenylisodecyl Phosphite	0.227
HALAR - Trilauryl Phosphite	0.263
HALAR - WESTON TP-24	0.263
HALAR - WESTON 465	0.227
HALAR - WESTON 467	0.238
HALAR - 10% $\text{SnO}_2 \cdot x \text{H}_2\text{O}$	0.083
PCTFE - 10% WESTON TP-24	0.389
PCTFE - Trilauryl Phosphite	0.20
PCTFE - 10% $\text{SnO}_2 \cdot x \text{H}_2\text{O}$	0.227
HALAR - 10% $\text{SnO}_2 \cdot x \text{H}_2\text{O}$	SE-3"
HALAR - 10% Stannous Oxalate	SE-2.5"
HALAR - 10% Stannous Oxalate	SE-3"
HALAR - 15% Stannous Oxalate	SE-2"
HALAR - 15% Stannous Oxalate	SE-1-3/4"
HALAR - 15% Stannous Oxalate	SE-1-1/2"
HALAR - 10% Stannous Phosphate	SE-2-1/4"
HALAR - 10% Stannous Phosphate	SE-2-1/4"
HALAR - 15% Stannous Phosphate	SE-2"
HALAR - 5% Stannous OXalate - 5% $\text{SnO}_2 \cdot x\text{H}_2\text{O}$	SE-3"

Note: 1. WESTON TP-24, 465 and 467 are orgnophosphorous flame-retardants
 Supplied by Weston Chemical Corporation and contain 23.5%,
 9.2% and 7.7% phosphorous respectively.

2. SE: Self-Extinguishing

TABLE II
Effect of Additives on Oxygen Index of HALAR

I. OI of HALAR Control = 58

2. At 5% Levels:

<u>Additive</u>	<u>OI</u>
Hydrated Tin Oxide	80.5
Stannous Oxalate	77
Stannous Phosphate, Tribasic	87
Stannous Pyrophosphate	80
Antimony Trioxide	69

3. At 10% Levels:

<u>Additive</u>	<u>OI</u>
Hydrated Tin Oxide	84
Stannous Oxalate	> 95
Stannous Phosphate, Tribasic	> 95
Stannous Pyrophosphate	82
Antimony Trioxide	70
Red Phosphorous	44

TABLE III
NASA FLAMMABILITY TEST RESULTS
Polymers Without Additives

<u>Polymer</u>	<u>Flame Propagation Rate, Inches/Second</u>	<u>Comments</u>
PCTFE	0.263	B-
VK	0.20	B-
TVS	0.277	B-
G-80	0.185	B-
HALAR	0.217	B-
C-E-C	0.294	B-
CM-1	0.214	B-
T-E	0.333	B-
FEP	0.227	B-
PFA	0.227	B-
XP-C1	0.277	B-

B- Entire 5" length of film specimen completely burnt.

TABLE IV
SYNTHESIS DATA ON C/T COPOLYMERS

<u>Copolymer Composition (Molar Ratio C/T)</u>	<u>M.Pt. (°C)</u>	<u>C_S[*]</u>	<u>MI^{**}</u>	<u>Extrudate at $\dot{\gamma} \simeq 200$ Sec. ⁻¹</u>
45/55	247	3.0	0.19	Slight melt fracture at 320°C.
45/55	247	4.0	0.35	Free of melt fracture at 320°C.
45/55	245	6.0	0.64	Slight melt fracture at 320°C.
50/50	240	5.0	0.61	Free of melt fracture at 300°C.
50/50	240	7.2	1.60	Free of melt fracture at 300°C.
50/50	238	9.4	3.5	Free of melt fracture at 300°C.
55/45	232	3.0	0.50	Slight fracture at 300°C.
55/45	232	6.0	1.60	Smooth extrudate at 300°C.
60/40	230	3.0	0.50	Smooth extrudate at 300°C.
60/40	227	7.5	4.3	Melt fracture at 300°C.
70/30	221	3.2	1.75	Severe melt fracture at 300°C.

*Conc. of chain-transfer agent (cc/100 gms total monomer)

**MI: Melt Index at 300°C/2,160 gms.

: Shear Rate

TABLE V

UPWARD FLAME PROPAGATION RATE TEST RESULTS ON CTFE/TFE
COPOLYMERS PER MSC-PA-D-67-13, CATEGORY A

<u>Copolymer Composition</u> <u>Mole Ratio CTFE/TFE</u>	<u>Test Results*</u>
100/0	B-
85/15	B-
75/25	B
70/30	SE in 3"
65/35	SE in 3"
60/40	SE in 3"
50/50	SE in 2-3/4"
45/55	SE in 3"
40/60	SE in 3"
30/70	B-
0/100	B-

*B: Burns more than 3"

*B-: 5" Length of film specimen completely burnt

*SE: Self-extinguishing

TABLE VI
TGA DATA ON DIFFERENT POLYMERS

<u>Polymer</u>	<u>LOI*</u>	<u>NASA Rating</u>	<u>%Weight Loss in N₂ at 425°C</u>	<u>%Weight Loss in O₂ at 425°C</u>
CTFE/Ethylene Copolymer	60	3	47	75
CTFE/TFE Copolymer	95	1	70	16
PCTFE	>95	4	91	99
PTFE	95	2	20 (at 550°C)	35 (at 550°C)

(TGA run on programmed heating rate of 200°/minute)

*LOI: Limiting oxygen Index

TABLE VII
SUMMARY DATA
RAM-EXTRUDER SPINNING TRIALS ON C/T POLYMERS

Sample No.	Composition CTFE/TRE	M.pt (°C)	Melt Index 300°C/216 gms	EXTRUSION RESULTS
C/T-13	50/50	240	0.61	O.K. at 310°C/0.6 gpm (Slight orange-peel melt fracture).
C/T-20	50/50	240	1.60	O.K. at 310°C, 400 sec ⁻¹
C/T-16	50/50	240	4.0	O.K. at 310°C/0.9 gpm; Cold-drawn 5:1, could not draw hot. UTS = 0.52 gpd; UE = 16.2%; TM = 11.6 gpd.
C/T-14	50/50	237	15.0	Free-flow at 300°C.
C/T-26	55/54	232	0.50	M.F. at 320°C/0.5 gpm.
C/T-22	55/54	232	1.60	O.K. at 310°C/0.9 gpm; Cold drawn 5.2:1; Could not draw hot. UTS + 0.66 gpd; UE: 28.7%; TM = 9.2 gpd
C/T-27	60/40	231	0.50	M.F. at 310-330°C/0.5 gpm
C/T-30	45/55	247	0.35	M.F. at 320°C/0.5 gpm.
C/T-31	45/55	247	0.20	Severe M.F. at 325°-350°C

TABLE VII (contd.)

<u>Sample No.</u>	<u>Composition</u> <u>CTFE/TFE</u>	<u>M.pt</u> <u>(°C)</u>	<u>Melt Index</u> <u>300°C/2160 gms</u>	<u>EXTRUSION RESULTS</u>
C/T-32	45/55	245	0.70/	Could be extruded and melt-drawn; could not be oriented at 25°C to 150°C
C/T-33	45/55	249	1.5/	Could be extruded and melt drawn; could not be oriented at 25°C to 150°C
C/T-36	55/45	234	0.80/	Orange-peel melt fracture.
C/T-37	50/50	240	1.15/	Could be extruded and melt drawn 10:1 and oriented 4.8:1 at 100°C. UTS = 0.82 gpd.
C/T-38	55/45	324	0.65/	Melt fracture

TABLE VIIa
Programmed Thermal Gravimetric Analysis of
CTFE/TFE Copolymers in Nitrogen
(Heating Rate = 10°/min.)

<u>Copolymer Composition</u>		<u>Melt Index</u>	<u>350°C</u>	<u>% Weight Loss</u>		<u>450°C</u>	<u>475°C</u>	<u>500°C</u>
<u>Mole % CTFE</u>	<u>Mole % TFE</u>			<u>400°C</u>	<u>425°C</u>			
60	40	0.5	--	2	12	65	100	100
50	50	0.6	--	0.5	7	45	100	100
		1.6	--	1.2	8	54	100	100
45	55	0.2	0.2	1	6	42	99.8	100
		0.35	--	1.2	6.5	45.5	100	100
50	50	0.5 (Filament)	--	--	5.5	46	100	100

TABLE VIII B
Programmed Thermal Gravimetric Analysis of
CTFE/TFE Copolymers in Air
(Heating Rate = 10°/ min.)

<u>Copolymer Composition</u>		<u>Melt</u> <u>Index</u>	<u>% Weight Loss</u>					
<u>Mole % CTFE</u>	<u>Mole % TFE</u>		<u>350°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>475°C</u>	<u>500°C</u>
60	40	0.5	--	1.8	10	65	99.7	99.8
50	50	0.6	0.3	1.8	10.5	63	100	100
		1.6	0.5	2.0	9.5	54.5	100	100
		4.0	0.3	1.5	7	50	100	100
45	55	0.2	1	1.5	6	46.5	100	100
		0.35	1	1.5	4.5	37	100	100
50	50	0.5 (Filament)	0.5	1.5	8.5	61.5	100	100

TABLE IX A
Isothermal Thermal Gravimetric Analysis of
CTFE/TFE Copolymers in Nitrogen

<u>Copolymer Composition</u>		<u>Melt Index</u>	<u>% Weight Loss</u>			
<u>Mole % CTFE</u>	<u>Mole % TFE</u>		<u>At 310°C</u>		<u>At 350°C</u>	
			<u>5 Min.</u>	<u>10 Min</u>	<u>5 Min.</u>	<u>1 Min.</u>
60	40	0.5	0.6	0.6	0.6	0.8
50	50	0.6	0.6	1.0	0.8	1.0
		1.6	0.6	0.8		
		4.0	0.6	0.7		
45	55	0.2	1.0	1.0	0.8	0.8
		0.35	1.0	1.2		

TABLE IX B
Isothermal Thermal Gravimetric Analysis of
CTFE/TFE Copolymers in Air

<u>Copolymer Composition</u>		<u>Melt Index</u>	<u>% Weight Loss</u>					
<u>Mole % CTFE</u>	<u>Mole % TFE</u>		<u>At 310°C</u>		<u>At 320°C</u>		<u>At 350°C</u>	
			<u>5 Min.</u>	<u>10 Min</u>	<u>5 Min.</u>	<u>10 Min</u>	<u>5 Min.</u>	<u>10 Min.</u>
60	40	0.5	--	--	1.0	0.8	0.95	0.75
50	50	0.6	0.6	0.6	0.6	0.6	0.6	0.75
		4.0	0.9	0.7				
45	55	0.2	0.4	0.4	0.75	0.75	0.8	1.0
		0.35	0.6	0.6				

TABLE X
Extension Thermomechanical Analysis
Data for 50/50 CTFE/TFE Copolymer Filament

<u>Run No.</u>	<u>%Longitudinal Change*</u>			
	<u>25-40°C</u>	<u>40-95°C</u>	<u>95-150°C</u>	<u>Overall 25-150°C</u>
1	0.18 (E)	0.22 (S)	0.42 (E)	0.38 (E)
2	0.55 (E)	1.13 (E)	0.59 (E)	2.3 (E)
3	0.34 (E)	0.22 (S)	0.53 (E)	0.65 (E)
4	0.14 (E)	0.03 (S)	0.63 (E)	0.74 (E)
5	0.31 (E)	0.09 (S)	0.51 (E)	0.73 (E)
6	0.05 (E)	0.16 (S)	0.48 (E)	0.37 (E)

* E: Elongation

S: Shrinkage

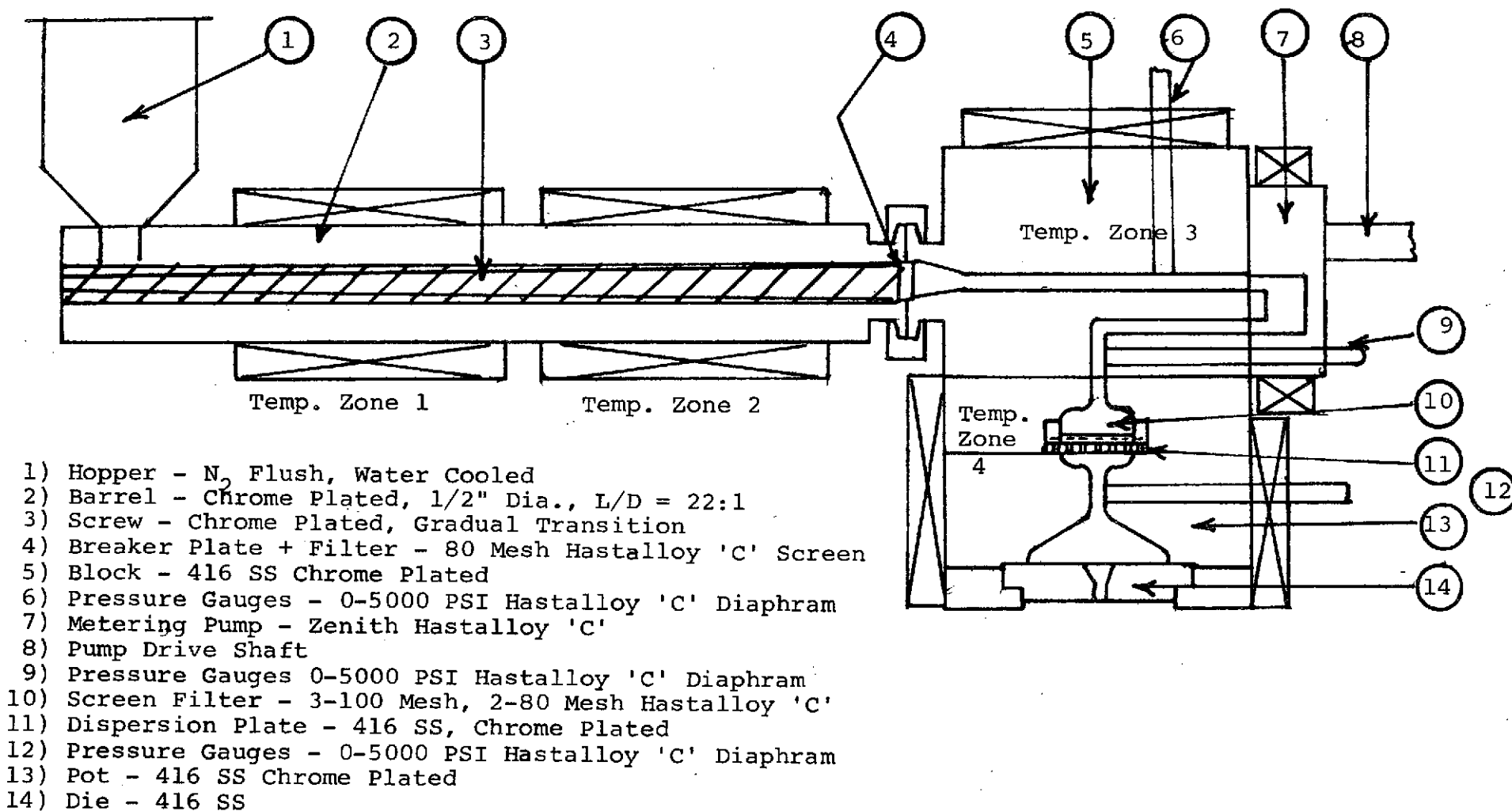
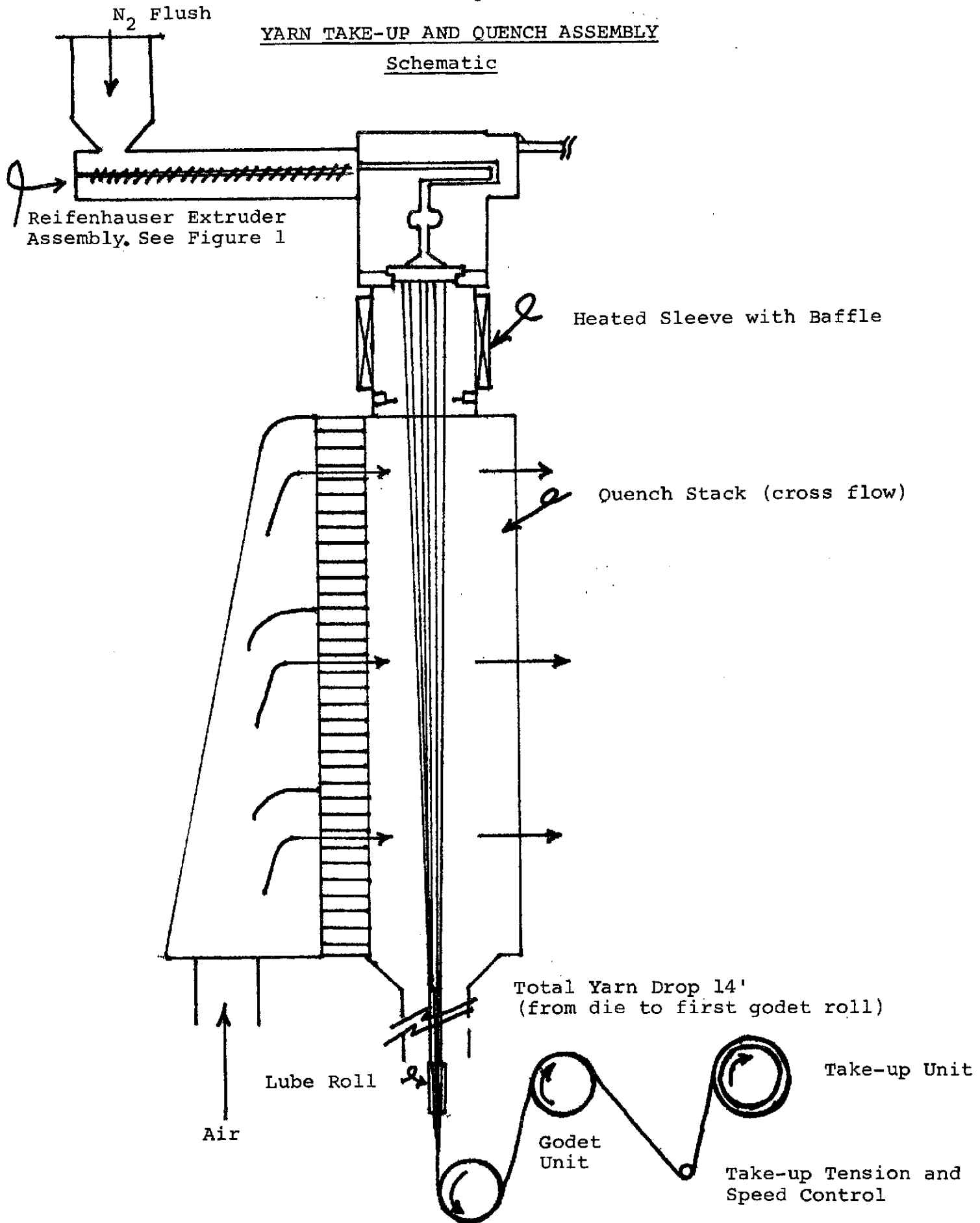


Figure 1 EXTRUDER ASSEMBLY

Figure 2



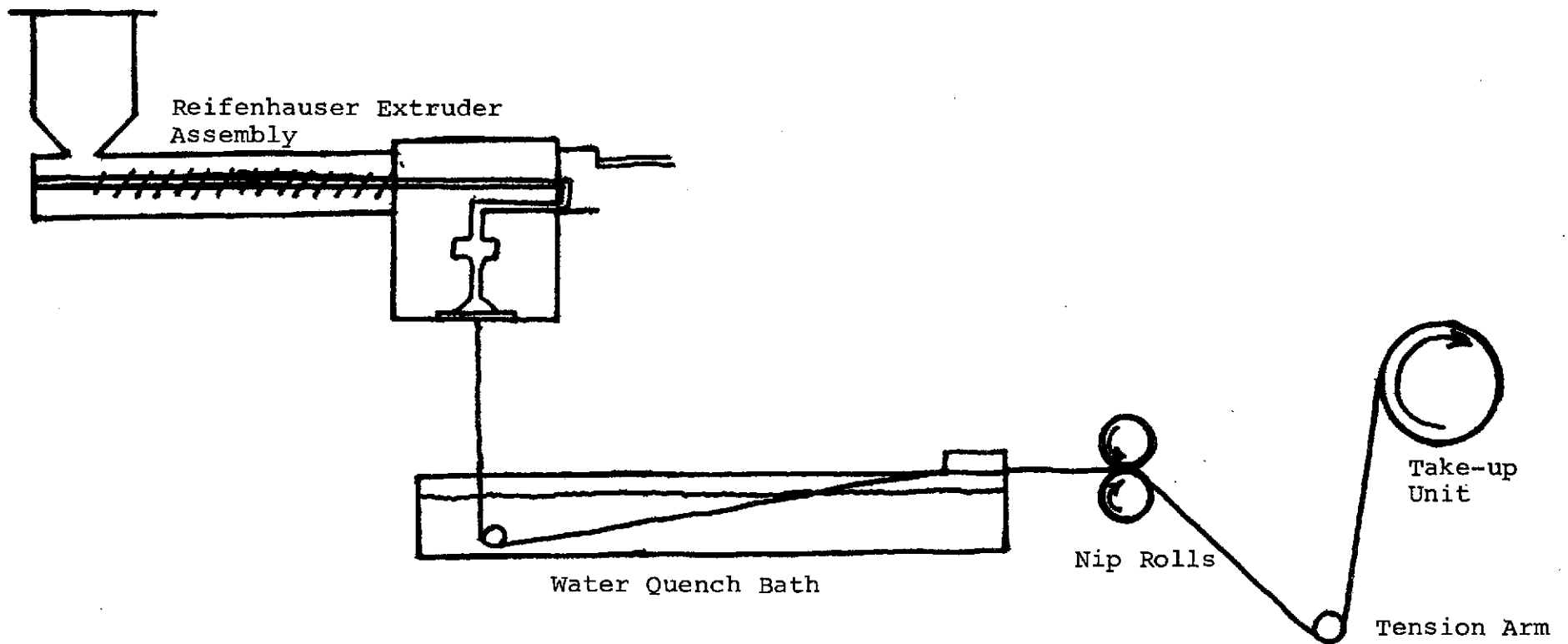


Figure 3 MONOFIL QUENCHING ASSEMBLY AND TAKE-UP ASSEMBLY

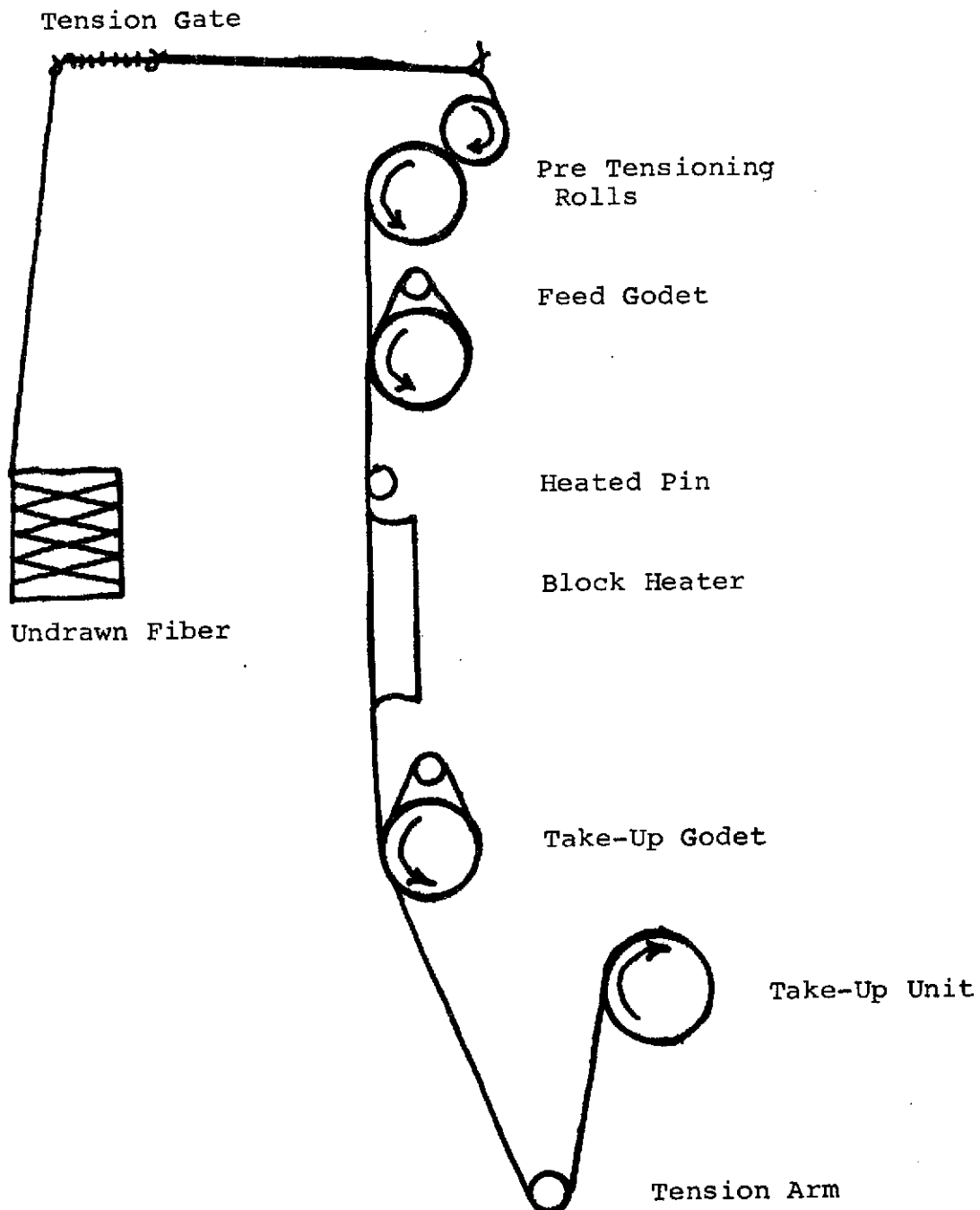


Figure 4 AIR DRAWING ASSEMBLY

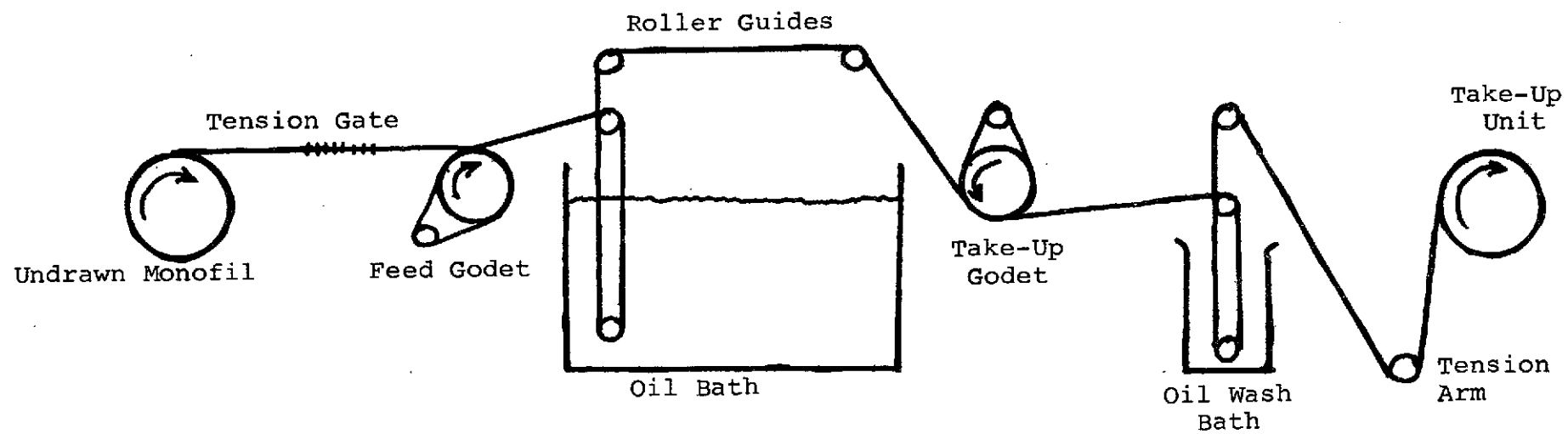


Figure 5 OIL DRAWING ASSEMBLY

PHASE II

A. Objectives

The identification of the ECS copolymer as an ideal candidate for eventual conversion into flame resistant fibrous materials led to the following objectives for Phase II:

1. Development of a feasible polymerization system for the ECS copolymer.
2. Development of a feasible polymer processing system.
3. Characterization and evaluation of selected copolymers.

B. Technical Approach

As described earlier the ECS copolymer of Phase I were produced by a bulk polymerization process. It is well known that high concentrations of uninhibited TFE, which must exist in a bulk polymerization, can spontaneously react, resulting in a high energy level explosion. Therefore this polymerization technique could only be safely used at the test tube level. Production of the ECS copolymer on a practical scale required the development of an alternate polymerization process.

The granular polymerization system, described below, was selected as the candidate with the highest probability of success. This decision was based on experience with other fluoropolymers, degree of operating safety and the relatively high level of possible control over key polymer variables. Because of subsequent success with this approach, other techniques, such as emulsion polymerization, were not experimentally evaluated.

Granular polymerization products must be washed (to remove catalyst salts), dried and possibly milled to a uniform particle size. The technology for conducting these unit operations exists. However some modifications have generally been required for each specific plastic. The reasons for this include varying impurity levels and differences in the physical structure of polymer solids exiting from the polymerization reactors.

Processing efforts, in the case of ECS, were concentrated on thoroughly washing and drying the polymer so that clean and bubble-free test specimens could be prepared.

Characterization of the ECS copolymer consisted of measuring key properties in the categories of physical, thermal, mechanical, electrical and chemical resistance testing. The effect of copolymer composition was determined by testing 40, 50, and 60 mol % CTFE copolymers. Other compositions were not evaluated since they failed to pass the NASA flame resistance test. The effect of molecular weight was determined by testing relatively low and high molecular weight copolymers.

C. Polymerization Research

The System

All of the runs in Phase II were made in a three gallon, jacketed, glass-lined reactor equipped with a turbine agitator. The glass lining is preferred over metals because of its superior resistance to corrosion and polymer build-up. Reactor temperature was monitored by thermocouples located in a thermowell suspended inside the reactor. The flow rate of brine, through the reactor jacket, was automatically controlled so as to maintain a constant reaction temperature. A pressure control system was also employed to insure a constant reaction pressure.

A turbine agitator, coated with CM-1 fluoropolymer, was centrally located to provide proper fluid mixing. CM-1, an Allied fluoropolymer, was used because of its resistance to corrosion, abrasion and polymer build-up.

A separate 9 gallon pressure vessel was used as a feed tank. Feed comonomer mixtures were prepared by adding CTFE and then TFE (gases) through a mixing nozzle. Gas sampling points were located at both the reactor vapor space and the feed tank.

Catalyst solutions were added to the reactor during a run (when required) by means of a positive displacement, constant rate pump.

General Procedure

The reactor was charged with 5 liters of deionized water, evacuated, purged with nitrogen and heated to the reaction temperature. CTFE, TFE and nitrogen were then added to the specified partial pressures. The feed tank was prepared as described above. Catalyst solutions were then added and the run was initiated. The run was controlled at constant temperature, pressure and agitation rate until 2-3 pounds of copolymer had been produced. This was determined by recording the decrease in comonomer supply in the feed tank.

At the end of a run the reactor was vented and purged with nitrogen. The product was discharged as a white, solid, granular powder. This powder was separated from the reactor water, washed and dried.

Agitation

The rate controlling factor, in polymerizations of this type, is the rate at which vapor space monomer can be transferred to the surface of the growing polymer particles (reaction site). The principal resistance to mass transfer is the bulk aqueous phase. This resistance can be minimized by operating at an agitation rate such that the aqueous phase is in a state of fully developed turbulent flow.

The Reynolds number, $Re = \frac{D^2 N \rho}{u}$ is a measure of the degree of turbulence. Fully developed turbulent flow occurs at $Re = 10^4$. The ECS reactor, operated at 500 RPM, resulted in a $Re = 1.8 \times 10^4$. Thus fully developed turbulent flow was assured.

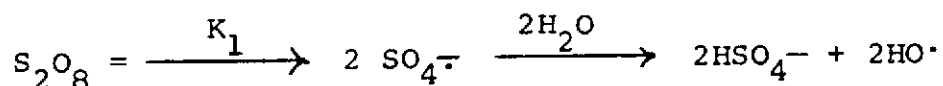
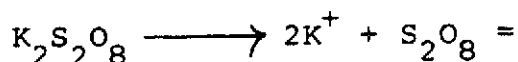
Catalyst System

The catalyst system consisted of potassium persulfate and sodium bisulfite. At reaction temperatures of 55°C or higher, free radicals were generated by thermal decomposition of potassium persulfate at a rate sufficient to maintain an adequate rate of polymerization without the need of a reducing agent. In this case the potassium persulfate solution was introduced into the reactor after the reactor had been charged and was up to temperature.

At reaction temperatures below 55°C, the decomposition of the potassium persulfate was induced with sodium bisulfite (a redox system). In this case the potassium persulfate was dissolved in the water first charged to the reactor and the sodium bisulfite solution was introduced into the reactor after the reactor had been completely charged. This solution was continuously pumped into the reactor at a very slow rate during the reaction.

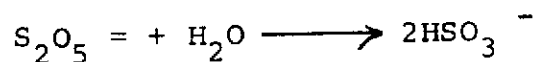
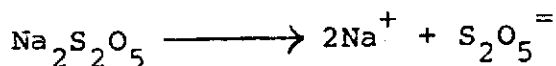
Several catalyst decomposition mechanisms have been proposed. The mechanism presented below has been considered to be the most likely (based on the results of previous internal research programs).

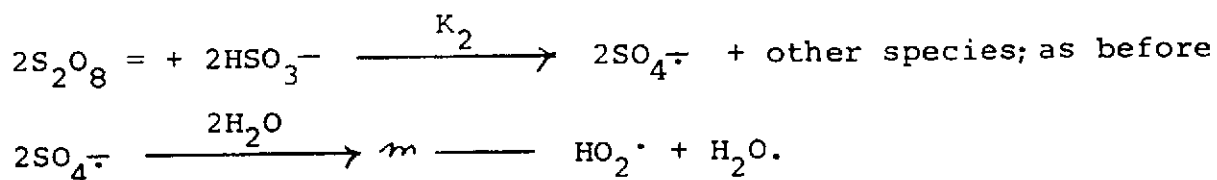
Potassium Persulfate - Only



By this mechanism the most probable dominating free radical is HO_2^{\cdot} and the most likely polymer chain end group is $-COOH$.

Persulfate + Bisulfite

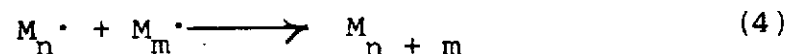
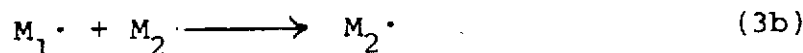




The controlling rate constants, K_1 and K_2 , are temperature dependent. At the same temperature, $K_2 \gg K_1$. The rate of copolymerization, under otherwise constant conditions, will be proportional to the rate of free radical generation. Therefore, as stated above, the persulfate-bisulfite catalyst system was required to achieve the desired ECS copolymerization rate at temperatures below 55°C . Constantly adding the bisulfite resulted in maximum control over the radical generation rate.

Reactivity Ratio

The copolymerization mechanism was assumed to be similar to that given in many textbooks (presented below for review purposes).



Step (1) described the catalyst decomposition. In step (2) polymer radicals M_1^{\cdot} and M_2^{\cdot} were formed. Step (3) showed the various possible combinations during the propagation or polymer chain growth sequence. Step (4) represented chain termination resulting in "dead polymer".

In a given copolymer system the reactivity ratios described the preference of a chain radical (M_1^{\cdot}) for adding to a molecule of the same species (M_1) versus adding to a molecule of the second species (M_2). The larger the numerical value of the ratio, the greater the tendency to add to the same species.

In the ECS reactor comonomers were present as a vapor space mixture, as gases adsorbed on the solid polymer surface and to a negligible extent, as gases dissolved in the water. Reactor pressure was maintained constant by continuously adding a comonomer mixture, from an external feed tank, to

replace reactor comonomer consumed by polymerization. Under steady-state conditions, therefore, the copolymer composition equalled the feed comonomer composition.

The reactivity ratios related the copolymer composition to the reactor vapor space composition. Thus the vapor space was adjusted to a specific equilibrium (steady-state) composition at the start of a run. Only in this manner could a homogeneous copolymer be produced. These parameters were mathematically related by the classical copolymer equation:

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \left[\frac{r_1 \frac{M_1}{M_2} + \frac{M_2}{M_2}}{r_2 \frac{M_2}{M_2} + \frac{M_1}{M_2}} \right]$$

where m_1 and m_2 were mole fractions of CTFE and TFE, respectively, in the copolymer, M_1 and M_2 were mole fractions of CTFE and TFE, respectively, in the reactor vapor phase and r_1 and r_2 were the reactivity ratios of CTFE and TFE respectively. Substituting Y for $\frac{m_1}{m_2}$ and X for $\frac{M_1}{M_2}$ and re-arranging terms resulted in the following equation:

$$\frac{X}{Y} (1 - Y) = r_2 + r_1 - \frac{X^2}{Y}$$

This was a form of the straight line equation. Thus, the straight line graph of the equation gave a slope which was r_1 and a Y intercept which was r_2 .

Suitable coordinates for this calculation were obtained by selecting run conditions that produced copolymers of 25, 50, and 75 mole % CTFE. The runs were made at 35°C, employing the potassium persulfate and sodium bisulfite catalyst system. Reactor vapor space compositions were selected to produce copolymers of approximately the desired compositions. The comonomers added continuously during the reactions were mixed exactly to the desired copolymer compositions. At regular intervals during the copolymerizations the reactor vapor phase was analyzed. After several "turn-overs" the composition of the vapor phase remained constant. By material balance the final equilibrium vapor space composition was that required to produce the homogeneous copolymer of the composition represented by the continuously added premixed supply of comonomers. The results of these runs and calculations of the coordinates were shown in Table XI. Figure 6 showed the straight line plot of the coordinates giving an r_1 (CTFE) of 3.2 and r_2 (TFE) of 0.82.

Copolymer Composition Curve

From the values of r_1 and r_2 , could be constructed a homogeneous copolymer composition curve, as shown in Figure 7, which provided the required vapor space composition for any copolymer composition. This curve was constructed by substituting r_1 and r_2 in the following form of the basic copolymer equation.

$$a = \frac{A(r_1 A + 1 - A)}{r_2 (1 - 2A + A^2) + A (2 + r_1 A - 2A)}$$

where a = mole fraction of CTFE in the copolymer:

A = mole fraction of CTFE in the vapor space.

Polymerization Rates

Using the copolymer composition curve, reaction conditions were set-up to produce homogeneous copolymers of various CTFE compositions at temperatures of 35°C to 60°C. Fixed polymerization conditions were:

Reactor Size	= 3 gallons
Water	= 5 liters
Agitation Rate	= 500 RPM
Nitrogen Blanket	= 65 PSIA
Total Pressure	= 165 PSIA

Figure 8 represented a typical reaction rate curve for a run at 45°C to produce a 50% copolymer. The constantly decreasing reaction rate (from a maximum at the start) was characteristic of all ECS runs, and was anticipated for this system.

The reaction rates listed in Table XI appeared to be (generally) less than the target minimum of 0.20 pounds/hour/gallon. These overall reaction rates, however, included the last portions of the polymerizations, in which the rates were quite low. As indicated on Figure 8, a more economical run time would have been 10 hours with an overall rate of 0.265 pounds/hour/gallon.

Basis Copolymer Data

The crystalline melting point of the ECS copolymers was determined as a function of composition (Figure 9). The curve endpoints represented the melting points of the homopolymers, PTFE (327°C) and PCTFE (212°C). The melt index curve (molecular weight) for 50 mol % homogeneous copolymers, produced over a wide temperature range, was also determined (Figure 10). These runs were also made at different catalyst levels. The results indicated that the molecular weight was a function mainly of the reaction temperature. Thus, a melt index selected from the range of about 0.3 to about 15 could be produced simply by selecting the appropriate reaction temperature.

Molecular Weight Distribution

The problems encountered in Phase I of this project were attributed, in part, to a relatively broad molecular weight distribution. This resulted from a varying free radical flux as well as a non-constant comonomer feed composition. With the catalyst systems and procedures employed in Phase II a reasonably constant free radical flux was generated. This along with constant comonomer vapor space and feed compositions, yielded products with relatively narrow molecular weight distributions.

D. Polymer Processing Research

Washing

The ECS copolymers were discharged from the polymerizer as fine white powders contaminated with catalyst residues (inorganic salts). Complete removal of these residues was required in order that clean test specimens might be molded. Preliminary tests indicated that this objective would be best accomplished by employing a centrifuge into which deionized water was constantly sprayed, and removed. The centrifuge, containing a polypropylene filter cloth, was operated at 700 RPM. Room temperature deionized water was continuously added at 10 gallons/hour. The conductivity of the exit water was periodically tested. A batch (3 pounds of polymer) wash was ended when the conductivity ~~reached~~ 1 part electotype per million parts of water.

Drying

All wet copolymers were transferred to glass trays and dried in an air circulating oven for up to 16 hours at 125°C. This procedure successfully produced bubble-free test specimens (bubbles in molded plaques generally indicated that the resin contained trace amounts of water).

E. ECS Engineering Properties

Critical engineering properties of selected ECS copolymers were measured. This data along with published values for the PCTFE and PTFE homopolymers were summarized in Table XIII.

Test Candidates (Table XIII A)

Test candidates included copolymers containing 40, 50, and 60 mol % CTFE. Copolymers, within this range, passed the NASA flammability test. Copolymers containing 50 mol % CTFE and of significantly differently molecular weights (Blends 1 and 4) were also evaluated.

The melt index of each of the candidates were determined under the same test conditions (275°C, 2160 gm load). The melt index was measured on samples extruded after a residence time of 6 minutes at 275°C. An indication of melt stability was obtained by measuring the melt index of the same material after a residence time of 30 minutes. Resin degradation would result in a color change (from clear to black) and a melt index number

significantly higher than the initial value (e.g. 6.0 vs. 2.0). All of the ECS candidates passed this test. It should be noted that these copolymers did not contain additives or stabilizers and that the melt index test error was ± 0.40 .

Mechanical Properties (Table XIIIB)

The mechanical properties were generally lower than expected. It was concluded that all of the candidates were of relatively low molecular weight. Copolymers of significantly higher molecular weight (produced in Phase I) have exhibited tensile strengths as high as 3600 PSI and elongations as high as 370%. However, these resins could not be converted into fibers by the techniques discussed earlier. The dynamic mechanical spectra of the ECS copolymers were compared to PTFE and PCTFE (Figure 11). The shear modulus of PCTFE was significantly higher than those for either PTFE or the four ECS blends below 40°C. Above 40°C the values were comparable. These curves did not show any appreciable effects of either changes in composition or molecular weight (within the regions explored) for the ECS copolymers.

Thermal Properties (Table XIIIC)

The relatively low heat deflection temperatures were also attributed to low molecular weight copolymers. The TGA curves (Figure 12) showed that the weight loss over the temperature range of 375° to 475°C, decreased with increasing TFE content. All of the candidates exhibited no weight loss up to 350°C. A sample of Blend 1 was heated in a stainless steel container (inside a tube furnace) to 475°C under vacuum. The pyrolysis products, after trapping in liquid nitrogen, consisted of 29 weight % gases and 71 weight % of low molecular weight waxes. The gases consisted of 10% TFE, 55% CTFE and 35% (by weight) of unknown compounds with higher boiling points than CTFE. The waxes contained a $-\text{CF} = \text{CF}_2$ group. Gas chromatographic and infra-red techniques were used for the gas and wax analysis. The observation of both monomer liberation and wax formation indicated that the degradation mechanism consisted of simultaneous chain unzipping and random chain cleavage.

Electrical Properties (Table XIIID)

The electrical properties of the ECS candidates were generally closer to PCTFE than PTFE. Changing the copolymer composition from 40 to 60 mol % CTFE did not significantly alter the electrical properties.

Chemical Resistance (Table XIIIE)

The candidates were immersed in solutions of the listed inorganic acids, bases and organic solvents for 12 days at room temperature. As expected the ECS copolymers were not attacked by the acids and bases and were only slightly swollen by trichloroethylene and ethyl acetate.

TABLE XI

<u>Run</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
<u>Vapor Space - Composition</u>				
- Mole % CTFE at steady state, M_1	29	29	18	56
- Mole % TFE at steady state, M_2	71	71	82	44
<u>Copolymer Composition (Monomer Added)</u>				
- Mole % CTFE, m_1	44	45	25	75
- Mole % TFE, m_2	56	55	75	25
$\frac{M_1}{M_2}, x$	0.408	0.408	0.219	1.275
$\frac{m_1}{m_2}, y$	0.786	0.818	0.333	3.0
$\frac{x}{y}$	0.519	0.498	0.657	0.424
$1-y$	0.214	0.182	0.667	-2
$\frac{x}{y} (1-y), \bar{y}$	0.111	0.096	0.438	-0.848
$-\frac{x^2}{y}, \bar{x}$	-0.212	-0.203	-0.144	-0.54

TABLE XII
POLYMERIZATION RUN DATA

Run No.	Temp. (°C)	CTFE (mol % in.)		Total Catalyst (gms/1 H ₂ O)		Product (gms)	Overall Reaction Rate (lbs./hour/gallon)
		Reactor	Feed	KPS	NBS		
21	35	30	45	4.79	1.69	795	0.054
22	35	30	45	9.54	1.68	795	0.055
23	35	30	48	14.10	2.42	722	0.050
24	35	20	25	14.10	2.42	1620	0.106
25	35	57	75	14.10	2.42	1100	0.037
26	45	30	50	4.79	3.38	2170	0.210
27	45	30	50	4.79	4.20	960	0.100
28	45	30	50	7.18	6.30	1420	0.125
29	50	30	50	3.76	3.30	1020	0.090
30	50	30	40	3.76	3.30	1380	0.165
31	50	30	50	3.76	3.30	1275	0.178
32	45	30	50	4.80	4.20	1350	0.141
33	60	30	50	4.0	0.0	1545	0.117
34	60	30	50	4.0	0.0	1400	0.112
35	55	30	50	8.53	0.0	1410	0.112
36	55	30	50	8.53	0.0	1220	0.098
37	50	40	60	3.76	3.30	1680	0.156
38	50	40	60	3.76	3.30	1590	0.167
39	50	25	40	3.76	3.30	1830	0.139
40	50	25	40	3.76	3.30	1700	0.135
41	35	30	50	4.79	4.20	1050	0.110

TABLE XIII A
ECS ENGINEERING PROPERTIES - TEST CANDIDATES

Item	Blend No. (1)		3	4
	1	2		
1. Polymerization Temp., °C	50	50	50	35
2. Composition, Mol % CTFE	50.0	60.0	40.0	50.0
3. Melting Point, °C	244.0	222.0	254.0	237.0
4. Melt Index, 275°C, 2160 gm load	2.2	12.0	1.5	0.1
5. Melt Index Stability (MI at 30 min.)	3.0	15.0	2.5	0.2
(1) Blended Runs = (see Table)	29	37	39	41
	30	38	40	
	31			

TABLE XIIIIB
ECS ENGINEERING PROPERTIES - MECHANICAL ⁽¹⁾

Test	ASTM No.	Blend No.		3	4	PCTFE	PTFE
		1	2				
1. Specific Gravity	792	2.170	2.171	2.181	2.167	2.1-2.2	2.14-2.20
2. Tensile Str., PSI	1708						
- Room Temp.		1,950	477	1,967	2,010	5,000	4,500
- 150°C		396	600	440	330	1,300	---
3. Elongation, %	1708						
- Room Temp.		25	3	13	17	150	300
- 150°C		14	5	10	41	750	---
4. Modulus, PSI	1708						
- Room Temp.		87,700	31,500	53,600	58,700	180,000	100,000
- 150°C		9,110	25,600	12,200	10,220	---	---
5. Compression Strength, PSI	695	2,530	---	2,150	---	6,000	1,700
6. Flexural Yield Strength, PSI	790	3,010	1,230	1,640	---	9,300	does not break
7. Flexural Modulus, PSI x 10 ⁻⁵	790	1.21	3.81	0.90	---	2.20	1.10
8. Impact Strength (notched Izod), ft. lbs./in.	256						
- Room Temp.		0.34	0.34	0.36	0.37	2.6	3.0
- -40°C		0.32	0.31	0.32	0.30	---	---
9. Tensile Impact, ft. lbs./in. ²	1822	23	8	66	73	275	350
10. Hardness, R	785	29	---	104	33	95	60 (D)
11. Abrasion Resist- ance, cc less/64 cycles	1242	0.869	---	0.642	---	---	---

⁽¹⁾ All tests at room temperature except where noted.

TABLE XIIIC
ECS ENGINEERING PROPERTIES - THERMAL

Test	ASTM No.	Blend No.			PCTFE	PTFE
		1	2	3		
1. Heat Deflection Temperature, °C	648					
- 264 PSI		58	---	55	---	---
- 66 PSI		132	---	112	258	250
2. TGA - % Weight Loss at: (1)						
- 350°C		0	0	0		
- 375°C		0.5	0.5	1.0		
- 400°C		1.5	4.5	2.0		
- 425°C		14.5	30.5	8.5		
- 450°C		77.5	87.0	55.0		
- 475°C		99.5	99.5	99.0		
- 500°C		99.5	100.0	100.0		

(1) 10°C/min. in air.

TABLE XIIIID
ECS ENGINEERING PROPERTIES - ELECTRICAL

<u>Test</u>	<u>ASTM No.</u>	<u>Blend No.</u>		<u>3</u>	<u>PCTFE</u>	<u>PTFE</u>
		<u>1</u>	<u>2</u>			
1. Dielectric Str.	149					
- Short-Time		450	439	463	550	480
- Step-by-Step		419	---	---	500	430
2. Dielectric Constant	150					
- 60 ³ Cycles		2.55	2.71	2.57	2.52	2.10
- 10 ³ Cycles		2.54	2.66	2.55	2.50	2.10
- 10 ⁶ Cycles		2.42	2.49	2.44	2.40	2.10
3. Dissipation Factor	150					
- 60 ³ Cycles		0.0033	0.009	0.007	0.0012	0.002
- 10 ³ Cycles		0.0044	0.010	0.006	0.0250	0.002
- 10 ⁶ Cycles		0.0167	0.016	0.015	0.0130	0.002
4. Arc Resistance, sec.	495	(1)	(1)	(1)	(1)	(1)

(1) Does not track or fail.

TABLE XIIIIE
ECS ENGINEERING PROPERTIES - CHEMICAL RESISTANCE

Test	ASTM	Blend No.		3	PCTFE	PTFE
	No.	1	2			
1. Weight Change (%) after 12 days at room temperature in:	543					
a) H ₂ SO ₄ , 96%		-0.007	-0.002	0.0	---	0.0
b) HCl, 37%		-0.003	+0.004	+0.002	0.0	0.0
c) HNO ₃ , 90%		+0.160	+0.033	+0.057	0.0	0.0
d) NaOH, 60%		-0.015	+0.118	+0.020	0.0	0.0
e) KOH, 60%		-0.012	+0.019	-0.013	---	0.0
f) Trichloroethylene		+0.230	+0.029	+0.149	+0.020	0.0
g) Benzene		+0.060	+0.030	+0.018	+0.600	0.0
h) Acetone		+0.100	+0.026	+0.087	+0.500	0.0
i) Kerosene		+0.010	+0.008	+0.002	---	0.0
j) Methanol		+0.020	+0.022	+0.035	0.000	0.0
k) Ethyl Acetate		+0.170	+0.104	+0.095	+6.00	0.0
l) Water		0.0	-0.004	-0.013	0.0	0.0
2. Tensile Strength, PSI	1708					
a) Control		1950				
b) H ₂ SO ₄ , 96%		2040				
c) HCl, 37%		1960				
d) HNO ₃ , 90%		1910				
e) NaOH, 60%		1960				
f) KOH, 60%		1950				
g) Trichloroethylene		1910				
h) Benzene		1950				
i) Acetone		1890				
j) Kerosene		2010				
k) Methanol		1950				
l) Ethyl Acetate		1860				
3. Elongation, %	1708					
a) Control		25				
b) H ₂ SO ₄ , 96%		26				
c) HCl, 37%		30				
d) HNO ₃ , 90%		24				
e) NaOH, 60%		12				
f) KOH, 60%		30				
g) Trichloroethylene		29				
h) Benzene		31				
i) Acetone		17				
j) Kerosene		26				
k) Methanol		28				
l) Ethyl Acetate		17				

FIGURE 6

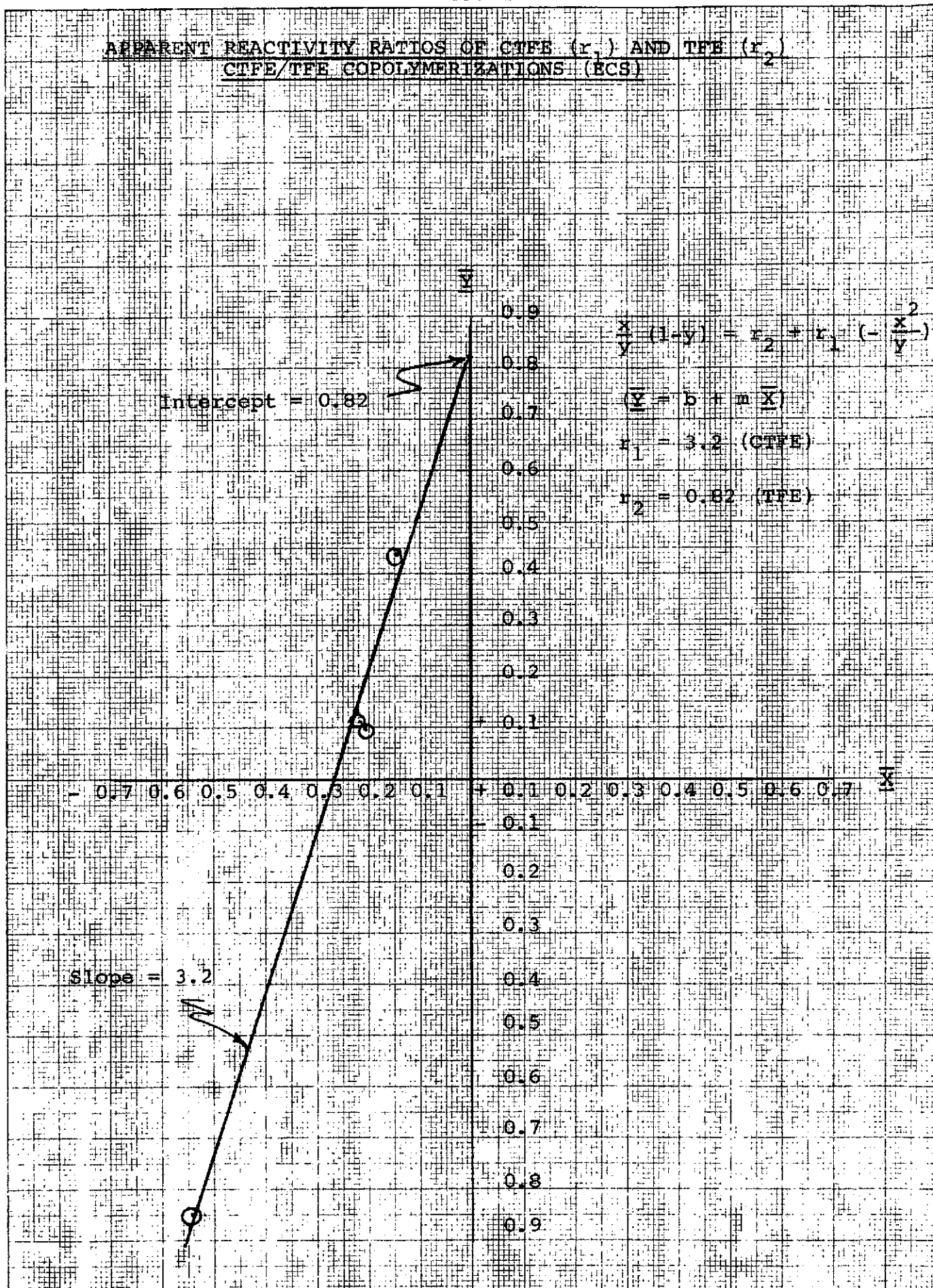


FIGURE 7

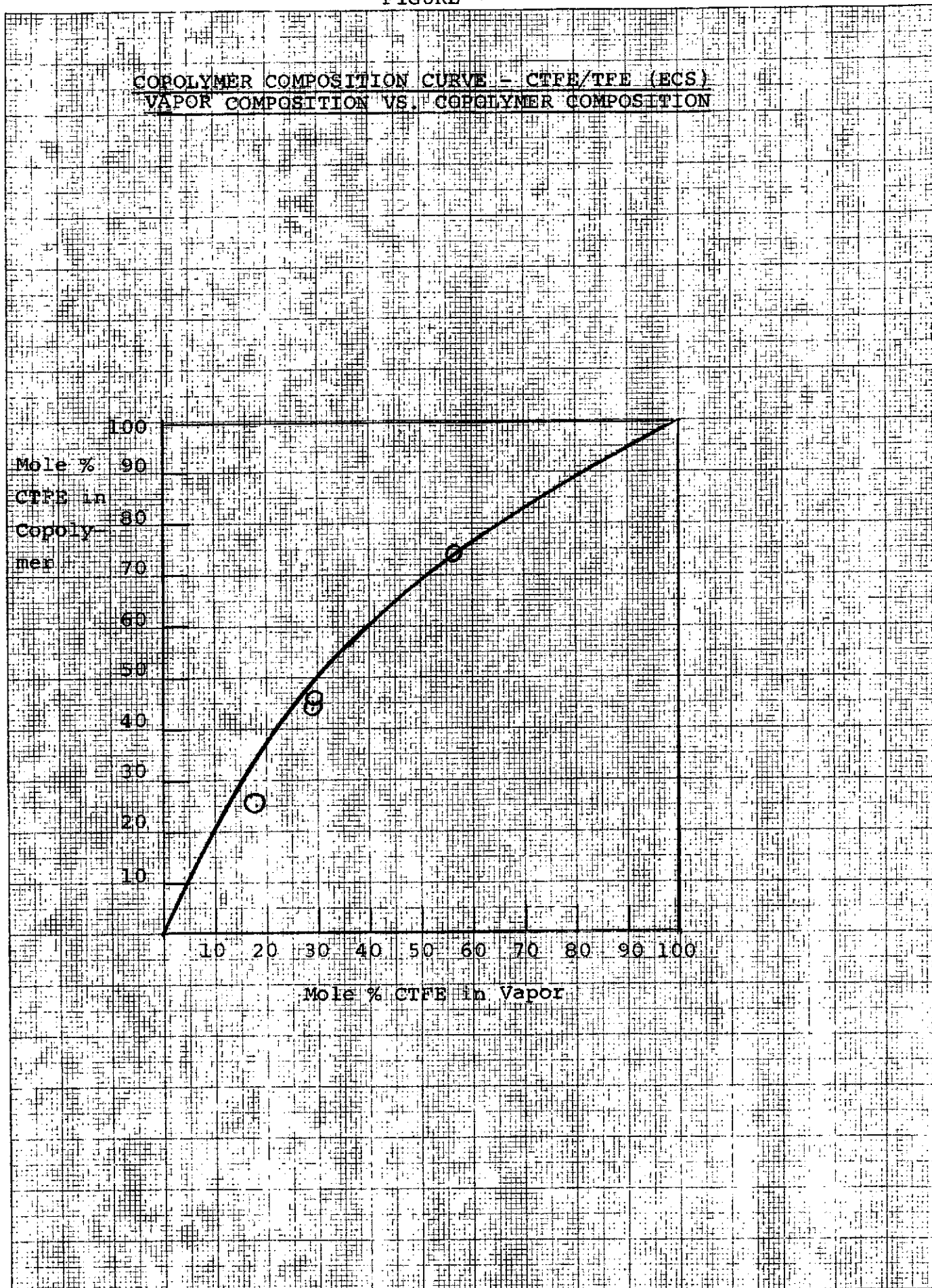


FIGURE 8

RATE CURVE: CTFE/TFE (ECS) COPOLYMERIZATION AT
50% COPOLYMER COMPOSITION, 45°C

Reaction Rate = 0.190 lbs./hr./gal. for 20 hours
Reaction Rate = 0.265 lbs./hr./gal. for 10 hours

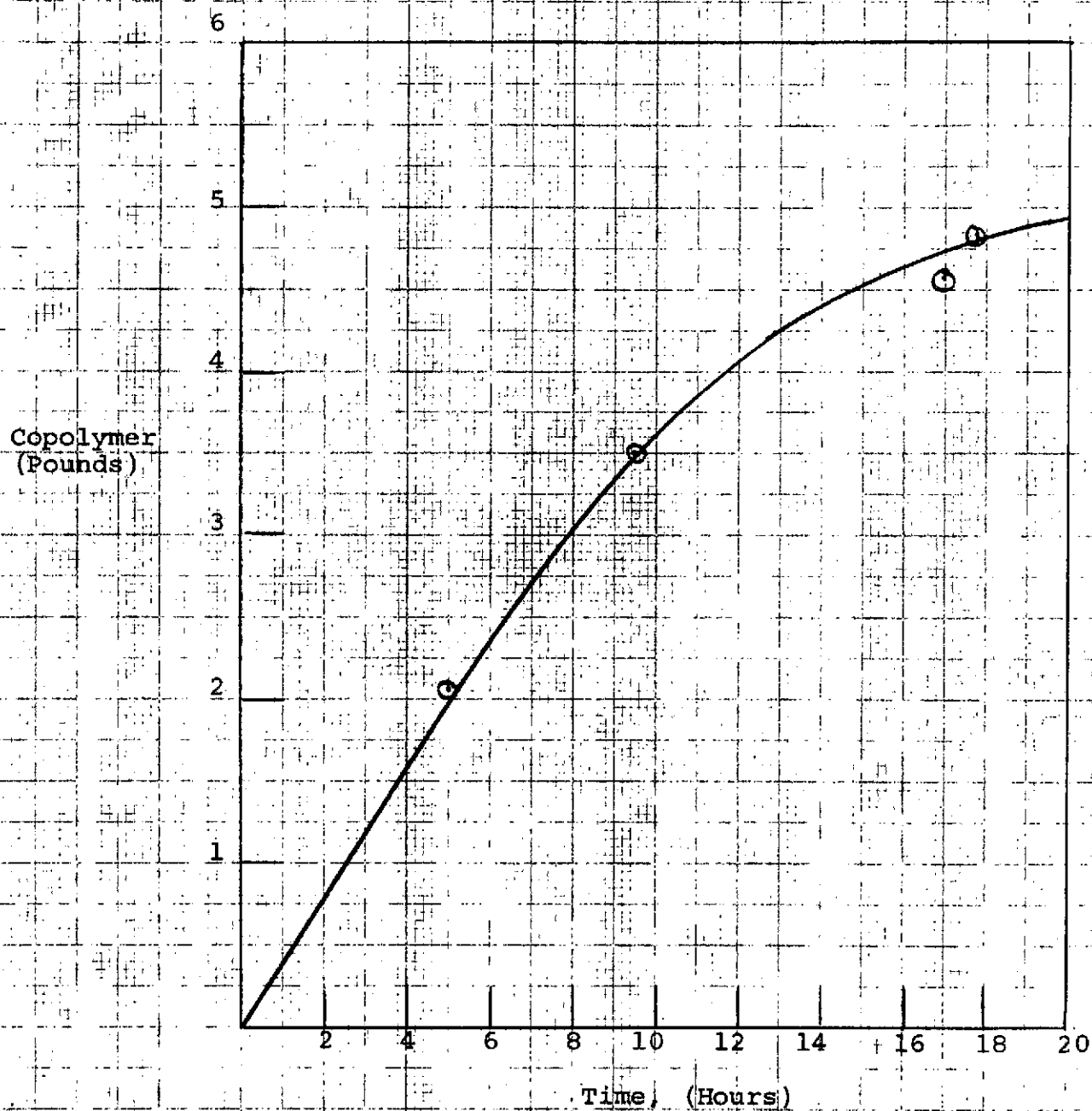


FIGURE 9

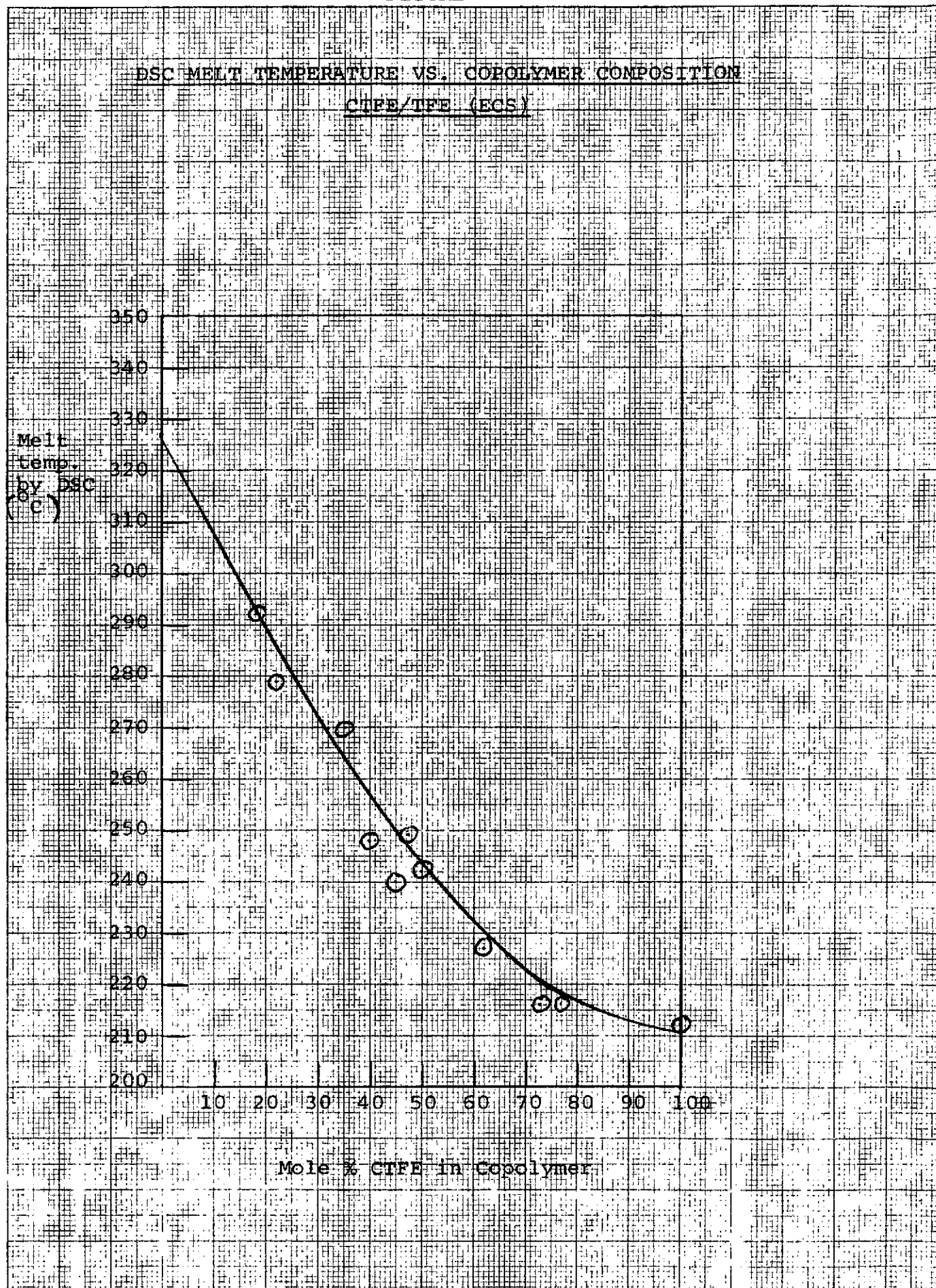
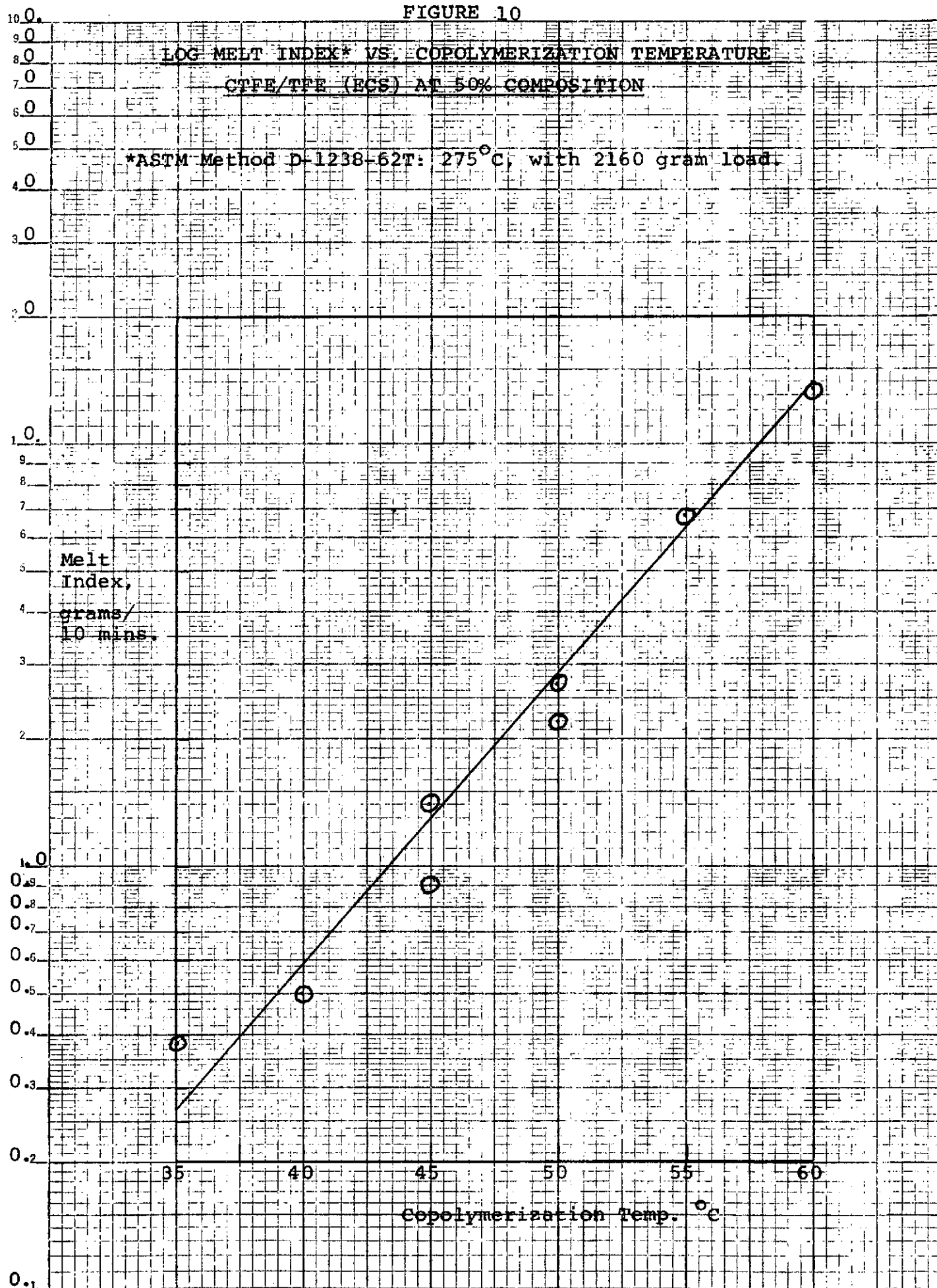


FIGURE 10



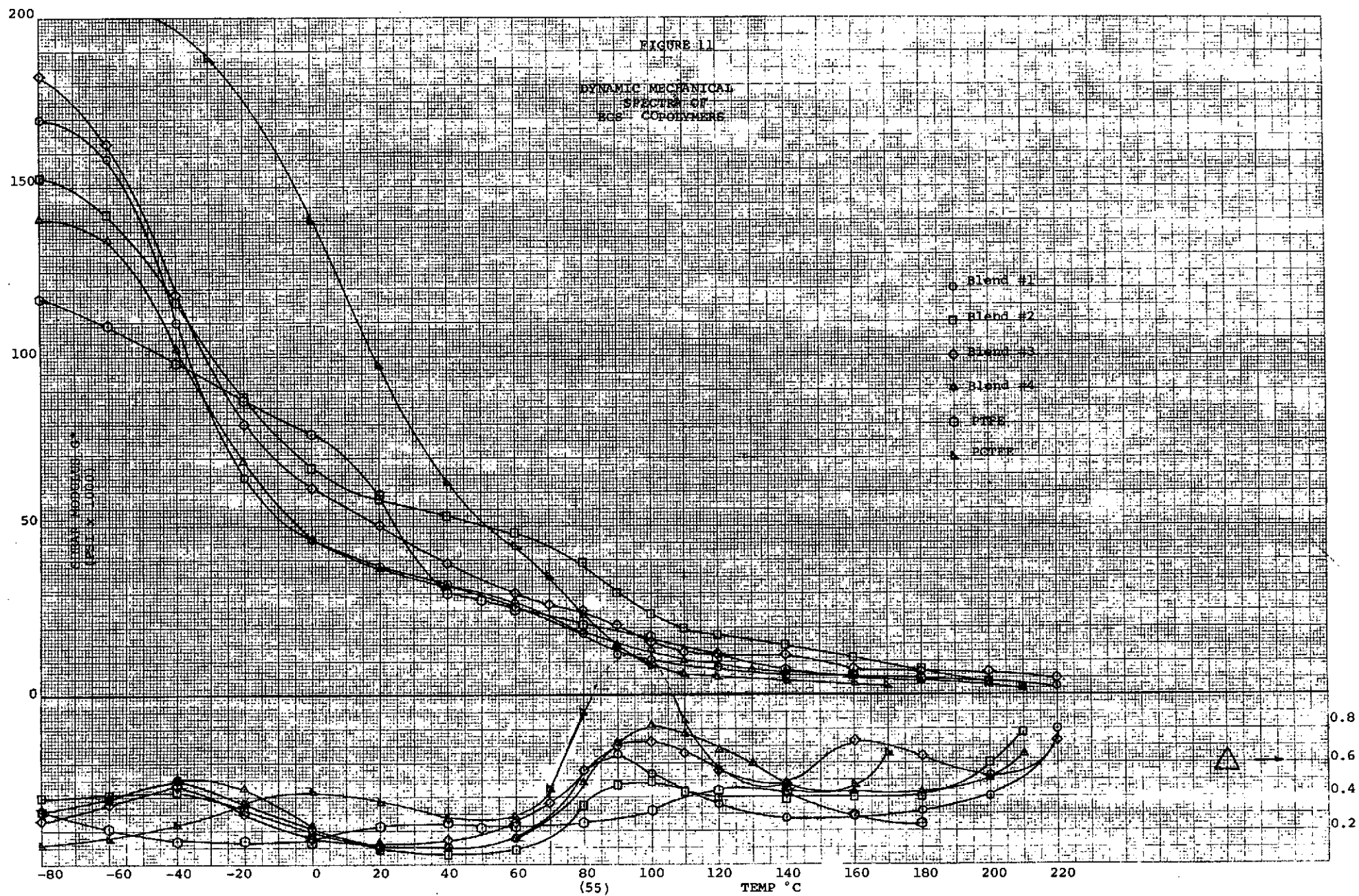
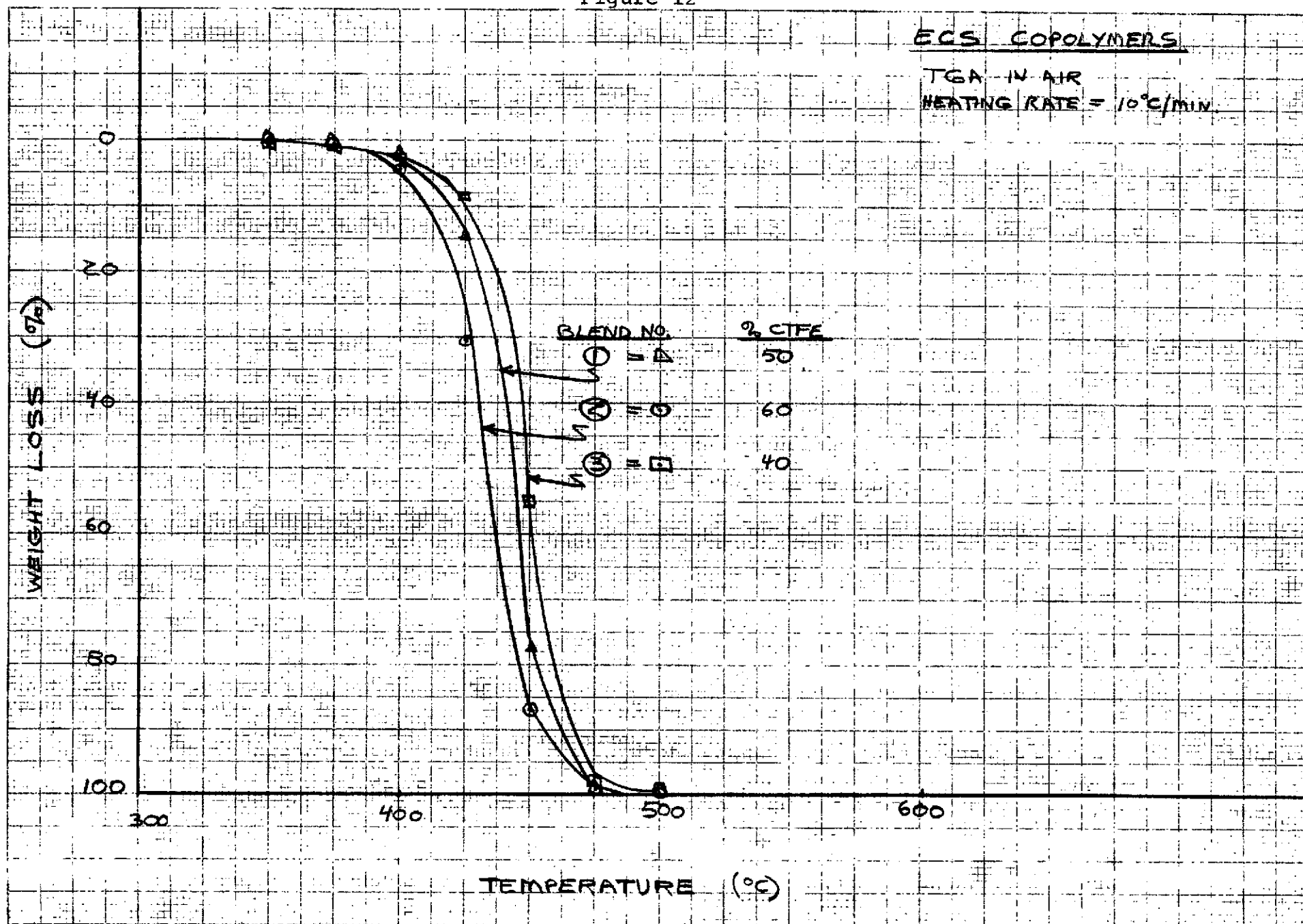


Figure 12



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APPENDIX . I .

- A. Upward Propagation Rate Test of
Category A, MSC-PA-D-67-13

TEST NO. 1
UPWARD PROPAGATION RATE TEST

PURPOSE

The purpose of this test is to identify spacecraft crewbay materials which allow the spread of fire.

TEST CONDITIONS - PRESSURES

The pressurized test environment for each material shall be determined from the applicable usage category and vehicle effectivity. The following table relates environmental tests conditions to category and module combinations.

<u>Category</u>	<u>Module</u>	<u>PSIA Oxygen</u>
A	CM	16.5
A	LM	6.2
C	CM	20.0
C	LM	8.7
G	CM and LM	16.5
H	CM and LM	14.7 PSIA AIR (unless otherwise specified)

TEST DISCIPLINE

Each test shall be directed by the cognizant Test Engineer or his appointed alternate.

The cognizant Test Engineer shall affix this signature to all test data sheets and verify adequate identification of test sample.

CRITERIA OF ACCEPTABILITY

Materials shall be self-extinguishing within three inches of the ignitor.

TEST EQUIPMENT

Test chamber shall have a volume sufficient to provide a minimum of 12 liters per gram of sample materials. It shall be suitably constructed and protected to insure safe operation. A window or viewing port for visual observations shall be included. The test chamber shall contain inlets for vacuum, an ignition wire, air, and oxygen. The chamber is to be fully protected against the possibility of operator injury in the event of explosive rupture.

Organic materials used in the construction of the chamber such as gaskets and seals shall be of types which contribute little or no outgassing to the chamber or which can be pre-outgassed by vacuum

cycling to a minimal identifiable amount, i.e., less than 10 ppm based on the chamber volume. A vertical sample holder shall be included and positioned within the test chamber.

Pressure Gauge - A pressure gauge capable of measuring absolute pressures with an accuracy of ± 5 Torr, or a pressure transducer and recorder with comparable capability shall be used. These gauges must cover the pressure range of the required test.

Oxygen Supply - The oxygen shall be commercially available oxygen conforming to specification MIL-O-27210, Type 1. Efficient and safe equipment shall be used for measuring the flow and for transferring the oxygen to the test chamber.

Sample Holder - The sample holder shall consist of a vertically mounted steel clamp which overlaps one fourth inch of each side of a specimen along the full five inch length of the sample, leaving a two inch wide by five inch long exposed center section.

Ignition Source - Ignition of the sample shall be accomplished by employing a regulated energy flux. The ignition source shall be a standard silicone ignitor placed within 0.15 ± 0.05 inch of the bottom edge of the sample. Both wire and paper shall contact with sample. The power supply to the wire shall provide sufficient voltage, controlled by means of a variable transformer, to ignite the silicone.

Propagation Rate Indicators - Motion Pictures - Motion picture records shall be kept of each burning test where appropriate.

In lieu of motion pictures, supporting data from a vertical bank of thermocouple indicators combined with a recorder may be used. However, a precision of at least five percent shall be obtained with the measuring device. If the thermocouples are used a minimum of four thermocouples shall be installed. Loss of more than one thermocouple or loss of either end point thermocouple shall invalidate the test.

SAMPLE PREPARATION

All material specimens shall be free of cuts, abrasions, or other flaws as determined by close visual inspection without magnification. Before the test the samples shall be cleaned by brushing or by flowing an inert gas over them to remove loose surface contamination.

Films and fabrics shall be tested in their "as received" condition. Specimens shall be cut out in the form of rectangles two and one half inches wide and five inches long. Foams or other thick materials shall be used in the applied thickness and be two and one half inches wide and five inches long.

Primers, coating materials, and paints shall be applied on the substrate material actually used in the spacecraft whenever possible. The coatings shall be applied in a thickness equivalent to normal usage and post cured in accordance with prescribed manufacturing practices.

Materials and components which will be used in an irregular size or shape shall be tested in the "as purchased" configuration. They shall be attached to the sample holder in such manner as not to affect the test results.

PRETEST PROCEDURE

Verify that all test equipment is in current calibration.

Verify oxygen certification (MIL-O-27210, Type 1)

Verify material identification by one of the following:

- Manufacturer's Certification
- NASA Certification
- Contractor Certification
- Definite Identification not Available

Prepare three samples per appropriate paragraph in Section above.

If irregularly shaped samples are tested, described the shapes.

Visually inspect each sample (There shall be no cuts, abrasions or other flaws).

Clean samples by brushing or by flowing an inert gas to remove loose surface contamination.

Weight the samples and record the weight.

Record the volume of the test chamber in liters.

Verify that the test chamber has a volume equal to or greater than 12 liters per gram of sample material.

Mount the sample in the sample holder and verify that the exposed center section is 2.0 ± 0.1 inches wide.

Position sample holder within the chamber.

Place the ignitor horizontally within 0.15 ± 0.05 " of the sample at the midpoint of its two inch width at the bottom.

TEST PROCEDURE

Evacuate the chamber to less than five (5) Torr.

Isolate the chamber and monitor pressure for one (1) minute. Testing may not begin until all leaks are corrected. (A leak is indicated if an increase in pressure of more than (1) Torr occurs.)

Pressurize the chamber to the required PSIA with oxygen.

After the chamber has stabilized at the test PSI, soak the samples for 10 minutes.

Verify chamber pressure is the test PSIA and isolate the chamber.

Start Motor Picture Camera and other applicable instruments.

Apply current to ignitor.

Record whether sample is self-extinguishing.

Note combustion characteristics (nature and color of flame, soot, residue and other pertinent observations).

Identify of the testing organization or agency.

Secure the chamber

REPORTING

Name of the material (generic).

Vendor designation and vendor.

Self extinguishing (yes or no).

Combustion Characteristics - Distance that flame progressed before extinguishing; flame phenomena and temperature; mass transfer by dripping, sputtering or sparking; etc.

Rate of pressure rise and final pressure.

Disposition or status, dimension, and size of sample material.

Name and number of test procedure.

Date of test.

Test Number

Identity of the testing organization or agency

Name of test conductor.

Names and signatures of Test Engineers.